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## XV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.

## A REVISION OF THE ATOMIC WEIGHT OF COPPER.

## FOURTH PAPER.

BY THEODORE WILLIAM RICHARDS.

Presented June 10, 1891.

## TABLE OF CONTENTS.

	PAGE		PAGE
Introduction . . . . .	240	II. Synthesis of Cupric Sulphate .	273
Balance and Weights . . . . .	242	III. Analysis of Cupric Oxide . .	276
I. Analysis of Cupric Sulphate . .	244	Tests for Impurities . . .	278
Materials . . . . .	245	Determination of Occluded	
Description: Three Series . .	249	Gases . . . . .	281
Cause of the Deficiency . . .	260	IV. Upon Typical Copper . . .	291
Atomic Weight of Sulphur . .	268	V. Summary of Results . . .	293
Atomic Weight of Copper . .	270		

## INTRODUCTION.

It will be remembered that recent investigation upon the atomic weight of copper has pointed toward the existence of a value for that constant very different from the one indicated by earlier determinations. During the winter of 1886-87 a number of experiments\* were made in this Laboratory upon the replacement of silver from solutions of argentic nitrate by means of metallic copper; and during the following winter these were supported by similar series† involving material from different sources. The consistent verdict of all these experiments indicated a considerably higher atomic weight than that which had previously been accepted; but although the new method seemed to be in every way satisfactory, the presumption must nevertheless remain in favor of the older value until the presentation of more evi-

\* These Proceedings, XXII. 342.

† These Proceedings, XXIII. 177; *Fres. Zeitschr.*, XXVIII. 392.

dence against it. Accordingly, another method of determination was devised, and the two distinct but concordant series of results obtained by this method fully confirmed the higher value. The aspect of the case was now wholly changed,—it presented two series of coincidences, of which one must necessarily be due to chance alone; and in such a case certainty can be reached only through a complete and intelligent reconciliation of the conflicting evidence. A careful examination of the possible sources of inaccuracy involved in all recent analyses failed to reveal the probability of a constant error greater than two or three units in the second decimal place. Therefore a complete examination of the older work seemed imperative, and the object of the present paper is to describe such a revision.

A brief review of earlier determinations is given in the first paper of the present series, but for the sake of convenient reference a complete summary is repeated below. On account of the present uncertainty with regard to the ratio of oxygen to hydrogen, the standard to which the figures in the following table are referred is the arbitrary one,  $O = 16$ ; and this standard has been adopted throughout the present paper.

*Atomic Weight of Copper.*

$O = 16.000.$

Berzelius, 1828, from CuO	Cu = 63.29
(Pogg. Ann., VIII. 182.)	
Erdmann and Marchand, 1844, from CuO	63.47
(J. pr. Chem., XXXI. 391.)	
Dumas, 1859, from CuO and Cu <sub>2</sub> S (?)	63.50
(Ann. de Chim. et de Phys., [3], LV. 129, 198.)	
Millon and Comaille, 1863, from CuO	63.12
(Compt. Rend., LVII. 147; Fres. Zeitschr., II. 474.)	
Hampe, 1874, from CuO	63.34
“ “ from CuSO <sub>4</sub>	63.32
(Fres. Zeitschr., XIII. 352; XVI. 458.)	
Baubigny, 1883, from CuSO <sub>4</sub>	63.47
(Compt. Rend., XCVII. 854, 906.)	
Shaw, 1886, through electrolytic equivalent	63.48
“ “ “ “ “ corrected	63.51
(Phil. Mag., [5], XXIII. 138.)	
Richards, 1887, 1888, by relation to Silver	63.60
(These Proceedings, XXII. 342; XXIII. 177.)	
“ 1890, from Cupric Bromide (two series)	63.61
(These Proceedings, XXV. 195.)	

The low value obtained by Hampe has been until recently universally accepted, because of the care employed in his analytical work, and the agreement between his results. Hence the present discussion will be confined almost entirely to the two substances which formed the bases of his operations.

The following values for the atomic weights of various elements entering into the present investigation will be assumed throughout the paper.

Oxygen	=	16.000	Hydrogen	=	1.008
Barium	=	137.10	Silver	=	107.930
Bromine	=	79.955	Sodium	=	23.053
Carbon	=	12.002	Sulphur	=	32.060

#### BALANCE AND WEIGHTS.

The balance used in the work to be described was made with especial care by Henry Troemner, of Philadelphia, and was procured particularly for the present research. The beam and pans are composed of aluminium, and all the remaining metal-work is plated with gold. By raising the centre of gravity, the pointer may be made to swing with great constancy as much as eight divisions of the scale for one tenth of a milligram; but since this degree of sensibility is far beyond the range of accuracy obtainable even in atomic weight investigation, the balance was usually adjusted so that the pointer moved ten divisions for a milligram. A reasonable increase in load altered this relation but slightly. The balance was kept in a small closet lined with curtains, and was protected as much as possible from changes in temperature. The air of the case was dried by means of potassic hydroxide and sulphuric acid, and large dishes of the former substance were kept in the closet outside.

The standard weights have already been described.\* They were carefully rubbed with chamois skin and again compared before the present work. The slight corrections, which differed scarcely at all from those previously found, were applied to each weighing.

A double rider attachment upon the balance made the method of weighing by substitution accurate and easy; and accordingly this method was invariably adopted, except in the first series of experiments upon cupric sulphate. In general, the vessel to be weighed was carefully tared with an adjusted set of common gilded weights, and the

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\* These Proceedings, XXV. 196.

vibrations of the pointer were noted. After the removal of the vessel standard weights were added to the left-hand pan until the same condition of equilibrium was reached. The vessel was then once more substituted for these weights, and any slight change of centre point was of course manifest at once. In the rare cases when such slight change appeared, the weights and vessel were alternately substituted for each other until constancy was reached. In the case of hygroscopic substances the already ascertained weights were first placed upon each scale pan, then the vessel was quickly removed from the desiccator and substituted for the standard weights, and, finally, the latter were again put in place.

All desiccators were allowed to remain in the closet with the balance three or four hours before the weighing, and objects were often weighed on successive days, to furnish assurance of constancy. In every case the barometer and thermometer were read, and any correction due to change of relative buoyancy amounting to more than the fiftieth of a milligram was applied to the result. With large vessels an invariable slight loss of weight, amounting sometimes to as much as one twentieth of a milligram, was noticed after the object had remained for some time upon the balance pan. The loss may have been due to the replacement of the perfectly dry air from the desiccator by the less completely dried air of the balance case. Possible error from this source was avoided by the employment of uniform conditions suited to the particular substance in hand.

All weighings were of course reduced to the vacuum standard by calculation from the specific gravities of the substances and weights involved.\* Through the great kindness of Professor Mendenhall of Washington, two of the Laboratory's ten-gram weights (one of brass and one of platinum) have been compared as carefully as possible with the standards of the Washington Bureau of Weights and Measures. Five comparisons of the Sartorius ten-gram weight with these gave the following results for its value in vacuum:—

1891.					Grams.
February 4.	By comparison with the brass weight,				10.00025
March 4.	“ “ “	platinum weight,			10.00025
March 14.	“ “ “	“ “			10.00026
June 12.	“ “ “	“ “			10.00026
June 12.	“ “ “	“ “			10.00024
Average,					10.00025

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\* These Proceedings, XXV. 196. Specific gravity of brass = 8.3.

The third and fifth of these comparisons were made with the balance in the condition of greatest sensibility, while the others were made exactly in the usual manner. It is not pretended, however, that all the weighings which follow have probable errors so small as these. The results are nevertheless an excellent gauge of efficiency of the balance, especially since the observations were made at widely varying temperatures and pressures. The correction involved, applying in the same proportion to all weighings, has been omitted from the following figures; but any weight given below may of course readily be reduced to the Washington standard by multiplication with the factor 1.000025.

#### I. THE ANALYSIS OF CUPRIC SULPHATE.

The only published analyses of cupric sulphate which have had for their object the determination of the atomic weight of copper are those previously mentioned. Hampe has very clearly described two extremely concordant electrolytic determinations of the copper contained in the so-called anhydrous salt. The greatest care had been taken to separate minute traces of metallic impurities from the preparation, which had been dried at 250° Centigrade; but apparently it was not realized that for the purpose in hand the retention of a trace of water by the salt was a much more serious possible cause of error than any other. Baubigny's analyses are less fully described, so that it is less easy to judge of their value. A different method, the conversion of cupric sulphate into the oxide by heat, was adopted for these experiments. The result was very different from that obtained by Hampe, but was more nearly accurate, because complicated with a less serious combination of constant errors.

The entire reconciliation of all these results, not only with each other, but also with the more recent analyses, involved the complete analysis and synthesis of cupric sulphate. A somewhat detailed account of the various operations is given below. Many of the less important points are necessarily omitted on account of the already too great accumulation of material, and many relations between the figures can be worked out by those whom they may interest. It is to be hoped that the effort to spare the overburdened literature of to-day any unnecessary additions may not have interfered with the clearness of the description. The first three series of experiments upon the analysis of cupric sulphate constituted a study of the effect of progressive refinement, and the first of the three perhaps hardly deserves a place in a paper upon atomic weights. Unless otherwise stated, the data are given in full.

*Materials used in the Analysis.*

*Cupric Sulphate.* — The substance used in the first series of experiments was partly prepared from very pure copper remaining from the cupric bromide research, and partly from other sources. It was perfectly neutral and reasonably pure. For the second and third series four hundred grams of the so-called “chemically pure” cupric sulphate of commerce were dissolved in a very large amount of water, and the solution was twice successively treated with a very small amount of potassic hydroxide in dilute solution; the mixture being occasionally shaken and allowed to stand each time for a week before decanting the clear supernatant liquid. One quarter of a gram of ammoniac bromide was added to this liquid; and after standing two weeks the solution was carefully filtered, evaporated to very small bulk in a porcelain dish, and again filtered from the deposited basic salt. The finely divided crystals obtained from this solution by agitation and cooling with ice were drained with a reverse filter,\* redissolved in hot water, and repeatedly recrystallized in platinum vessels. The first three mother liquors were rejected, but the later ones were all combined. After three more recrystallizations the substance contained in these mother liquors was dissolved in cold water and allowed to crystallize by slow evaporation in pure air. The preparation thus made was used in the second series of analyses.

The crystals obtained by eight successive crystallizations in platinum vessels were dissolved in cold water, and the salt was slowly recrystallized over sulphuric acid in a vacuum. The substance thus obtained was dissolved in water which had been distilled in a platinum retort, and after standing six days the perfectly clear solution was again brought to crystallization in a vacuum. These crystals were dried in a platinum dish over partially dehydrated cupric sulphate, and were used for the third series of experiments. The neutrality of each of these preparations was determined as nearly as possible by means of methyl orange, after the manner described in these Proceedings, Volume XXV., page 201.

*Sodic Carbonate.* — As sodic carbonate formed one of the chief bases for the determination of the sulphuric acid, its manufacture in a pure state was a matter of great importance. From the “chemically pure” material of commerce one may easily procure by five recrystallizations a material which gives no coloration with ammoniac sulphy-

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\* These Proceedings, XII. 124.

drate, nor, after neutralization, with potassic sulphocyanide.\* Sodic sulphate and chloride are even more readily separated than traces of iron.

Three separate preparations of sodic carbonate were used in the course of the work. For the first series of comparatively crude experiments the solution of ordinary "chemically pure" material, which almost invariably contains a perceptible amount of finely divided solid matter, was after filtration twice recrystallized in a platinum dish. It was subsequently found advantageous to prevent the clogging of the filter by two or three preliminary recrystallizations, in the course of which most of the solid matter finds its way into the mother liquor.

The second sample of sodic carbonate was recrystallized six times after filtration. The vessels, rod, and reverse filter were all of platinum, and water was used which had been distilled in a platinum retort.

Besides all these precautions, several additional ones were taken in the preparation of the purest sample of sodic carbonate designed for the third series. The water used had been distilled four times: first alone, next over potassic permanganate, then over acid potassic sulphate, and finally in a platinum still without the addition of foreign matter. Every precaution was taken to exclude dust and acid fumes, and the sodic carbonate was recrystallized ten times after filtration. The salt prepared in this way gives an absolutely odorless warm concentrated solution. The second and third samples gave essentially identical results. Each of the three preparations was pure snow-white, whether fused or unfused; each gave a perfectly clear and colorless solution with water; and not even the first gave the least test for hydrochloric or sulphuric acid.

On the other hand, as Stas has already indicated, the most elaborate precautions are unable to free sodic carbonate wholly from traces of silica and a basic oxide, which is probably alumina. The former impurity was determined in the usual manner. The alumina and silica were determined together in new portions of the salt by exact neutralization with hydrochloric or sulphuric acids, ignition of the evaporated product, and weighing of the insoluble residue. Phenol phthalein was used to determine the neutral point, and hence the

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\* Stas appears once or twice to have had more difficulty in accomplishing this result. At other times his experience seems to have coincided with that described above. Compare Aronstein's translation (1867), pp. 112, 270, with p. 275.



insoluble bases present were necessarily precipitated. It is needless to state that the operations were conducted in platinum vessels. Neglecting two determinations which were vitiated by known impurity, the weight of total residue obtained varied from 0.15 to 0.41 milligram, while the weight of sodic carbonate taken varied from 1.02 to 3.06 grams. The average of twenty determinations showed about thirteen parts of impurity to exist in one hundred thousand parts of the salt. Silica constituted about forty per cent of this impurity. The third specimen did not differ essentially from the second on these averages. Owing to the slight solubility of silica in sodic chloride solutions,\* the observed amount of this impurity may be slightly too low, but for the present purpose the correction is unimportant. The filter papers used in this part of the investigation left upon ignition an ash of 0.00004 gram.

Since the silica and alumina are probably present as sodic silicate and aluminate in the original carbonate, and may be considered as replacing carbon dioxide molecule for molecule, it is evident that the correction to be applied will not equal the whole weight of the residue. Upon this assumption the correction when phenol phthalein is used as an indicator amounts to about half the weight of the impurity, or about 0.007% of the weight of the sodic carbonate. Toward methyl orange aluminic hydroxide is alkaline; hence in this case the errors due to the two impurities tend to counterbalance each other, and the correction may be omitted. The presence of a small amount of alumina thus explains the slight difference observed later between the results obtained with these two indicators.

The crystallized sodic carbonate was dried over pure boiled sulphuric acid in a vacuum, and subsequently ignited to a dull red heat in a double crucible over a Berzelius spirit lamp. The latter apparatus was employed in order to avoid the possible introduction of impurity from illuminating gas. It was found that the salt could be ignited to perfectly constant weight at any temperature between dull redness and its fusing point. The light powder contracts and "sinters together" at a low red heat, and then remains essentially unchanged in weight until it melts. The unfused salt was not observed to gain perceptibly in weight upon an hour's exposure to the air of the balance case; upon the other hand, the fused salt, which of course was never used as a basis of determination, was markedly hygroscopic.

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\* Stas, Aronstein's translation, p. 279. In this place the correction is applied to sodic chloride, but not to the nitrate formed from it.

*Acids.*—The chemically pure hydrochloric and nitric acids were each distilled three times successively in a platinum still. Large quantities evaporated in open dishes left unweighable and scarcely visible residues. The insignificant amount of the residues was a proof of the purity of the air, as well as of the acids. Neither acid gave a test for iron, and the nitric acid contained no chlorine even at the beginning of the operations.

Since the platinum still was very large, it was found more convenient to distil sulphuric acid from a small hard glass retort heated by a ring burner, immediately before it was needed. After three such distillations, a preparation was obtained which left no weighable residue upon the evaporation of any quantity used in the work.

All sulphuric acid used for drying was boiled with ammoniac sulphate.

In order to keep the air of the laboratory quite pure, during the greater part of the time neither volatile acids nor ammonia were allowed in the room devoted to the investigation, and all available precautions were taken against dust.

*Indicators.*—As is well known, the salts of most of the heavier metals are acid toward phenol phthalein and neutral toward methyl orange. The most important consequence of this relation has already been pointed out. When the former indicator was used, the slightly acidified solution was of course first freed from carbonic anhydride by long continued heating upon the steam bath, and the end point was determined with pure caustic alkali. It is a noteworthy fact, that methyl orange is useless in very concentrated solutions of sodic sulphate, the color change becoming apparent only upon dilution. This indicator is naturally less serviceable in the presence of a strong color like that of a copper salt. It is less sensitive with cupric sulphate than with cupric bromide. In such cases as these, colorimetric comparison can alone afford accurate results; but even here the effect of a personal equation must be more or less perceptible.

Since the amount of either indicator used in any one case was not more than the thirtieth of a milligram, it could not have seriously influenced subsequent operations with the solution.

*Water.*—The distilled water taken hot from the tin-lined condenser around a steam-drying oven contained no ammonia discoverable by Nessler's reagent, and in the first crude experiments this water was used without further treatment. After having been once more dis-

tilled in a platinum still, it appeared to be very pure. The first portions of the distillate were rejected, although no ammonia was found in them. The water left absolutely no trace of residue upon evaporation, even after long standing. Such doubly distilled water was used in the second series of experiments.

For the third series all the water used, even for minor operations, was distilled four times: first alone, then over alkaline potassic permanganate, next over acid potassic sulphate, and finally once more alone in the platinum still. Since this water was not different in any of its properties from the second preparation, the last refinements were probably unnecessary; and in later work water which had been distilled only twice was used.

The value of the present work has been largely increased by the unlimited supply of platinum ware placed at the disposal of the writer through the kindness of Professor Cooke. Because of the large size of some of the retorts and bottles, it was impossible to free these vessels from iron after the method of Stas. Accordingly they were digested alternately with strong hydrochloric and nitric acids until pure acid which had remained in them for days gave no test for iron after evaporation upon the steam bath.

Smaller vessels were freed from iron in the usual manner, by treatment with the vapors of ammoniac chloride at a red heat, as well as with fused acid potassic sulphate. They were usually protected during ignition by an outer crucible, from which they were separated by a coil of platinum wire. Crucibles weighing twenty grams rarely showed a variation of more than one twentieth of a milligram between the weights taken before and after any ordinary operations, excepting when ignited with cupric oxide under conditions which will be explained later.

### *Description of Analyses.*

#### FIRST SERIES.

It is evident that the most probable constant error in Hampe's work lay in the great hygroscopic power of cupric sulphate dried at 250°. A possible means of detecting such error existed in the use of the crystallized salt as a starting point. This salt was therefore coarsely powdered, dried to constant weight over a mixture of crystallized and partially dehydrated cupric sulphate, and analyzed by electrolysis in the usual fashion. Although the crystalline powder must have contained occluded water, the quantity of copper found in

several samples from different sources was much larger than that demanded by the old atomic weight, and closely approached the theoretical quantity based upon the new value.

In the third experiment the weight of water lost by heating the salt to constant weight in the manner described by Hampe\* was also determined, and this amount proved to be nearly three tenths of a per cent less than it should have been according to any hypothesis. Since larger crystals of cupric sulphate exposed to air above the desiccating mixture already mentioned lost none of their lustre, and since the salt under these conditions comes to perfectly constant weight, it seemed highly probable that the apparent deficiency of crystal water was due to occlusion in the so-called anhydrous salt, and not to any previous efflorescence of the crystals.

The sulphuric acid produced during the electrolysis † was preserved in each case, and approximately determined by means of the first preparation of sodic carbonate; also afterwards by the evaporation of the solution of sodic sulphate. Since the manipulation was more or less imperfect, and the materials and water not quite pure, it is thought unnecessary to include these somewhat bulky data in full here, but the evidence which they furnished was conclusive upon one point. The percentage of acid was not equal to the complement of the other percentages. In other words, over one tenth of a per cent of material had not been determined.

	Found.	Theory Cu = 63.60.	Theory Cu = 63.33.
Percentage of Water . . .	35.958	36.0695	36.109
“ “ Copper . .	25.455	25.4665	25.385
“ “ SO <sub>4</sub> . . .	38.46±	38.464	38.506
Total . . . . .	99.87	100.000	100.000

It is seen that we are dealing, not with infinitesimals, but with grave error evident to the crudest analysis. The reason for the deficiency has already been suggested, but the proof is yet wanting.

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\* *Loc. cit.*

† In this connection it may be noted that Hart and Croasdale have quite independently used the sulphuric acid thus formed as a basis of alkalimetric analysis. (Chem. News, LXIII. 93, 1891.) The idea appears to be a good one

The ratio between the copper and the sulphuric acid, or rather between the copper and sodic carbonate on the one hand and sodic sulphate on the other, affords a new twofold basis for the calculation of the atomic weight of copper. This basis is entirely independent of the always uncertain weight of the cupric sulphate and the objectionable method of calculation from difference. The results correspond to the new atomic weight, but the complete discussion of this phase of the subject will be reserved until more definite data have been given. It is interesting to note that these comparatively crude experiments differ only by one or two units in the second decimal place of the result from the far more carefully executed work yet to be described.

ANALYSIS OF CUPRIC SULPHATE.—FIRST SERIES: DATA AND RESULTS.

*Weights reduced to Vacuum Standard.*

No. of Experiment.	Weight Cupric Sulphate (cryst.).	Weight $\text{CuSO}_4$ (250°) found.	Weight Copper found.	Per Cent Water lost at 250°.	Per Cent Copper.
1	2.8815	....	0.7337	....	25.462
2	2.7152	....	0.6911	....	25.452
3	3.4639	2.2184	0.8817	35.958	25.454
Average . . .				35.958	25.455

SECOND SERIES.

Although from the earlier experiments it appeared that the deficiency in the sum of the analytical results might be explained by the hypothesis of the existence of water in the so-called anhydrous cupric sulphate, it was possible that at least a part of this deficiency might be due to experimental error. The next step of the research was therefore to start again upon a more refined basis. It was important, too, that some proof of the above mentioned hypothesis more definite than an indirect inference should be obtained. The clearest idea of the various operations may probably be acquired through a detailed statement of one of the experiments, and accordingly such a statement is given below.

*Experiment 4.*—The cupric sulphate,\* having been cautiously powdered in an agate mortar and dried to constant weight over the desiccating mixture already described, was gradually heated to 255° in a platinum crucible with a very closely fitting lid.

\* See page 245 of this paper.

	Grams.
Weight of crucible + $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	= 23.36188
“ “ alone	= 20.30300
“ cupric sulphate in air	= 3.05888
Correction to vacuum (Sp. gr. = 2.274)	= .00118
Corrected weight $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , in vacuum	= 3.06006
Weight crucible + $\text{CuSO}_4$ dried for three hours at $255^\circ$	= 22.26243
“ “ dried for two hours more	= 22.26233

The crucible and contents gained in weight upon the balance pan at a rate of only one tenth of a milligram in four minutes, and hence the last weighing is without doubt sufficiently accurate. When the weight had thus become constant, twenty drops of strong pure sulphuric acid were added to the white powder, and the whole was kept at a temperature of  $365^\circ$  for three and one half hours in a suitable air bath composed of a nest of porcelain crucibles. An air thermometer was used in measuring the temperature.

	Grams.
Weight of crucible and contents	= 22.25905
The same, after reheating for four hours with six drops more of $\text{H}_2\text{SO}_4$	= 22.25900
Weight in air of cupric sulphate dried at $365^\circ$	= 1.95600
Weight in vacuum of cupric sulphate (Sp. gr.* = 3.61)	= 1.95637
Loss of weight between $255^\circ$ and $365^\circ$	= .00333

The crucible and contents gained in weight even less rapidly than before.

This experiment shows that the so-called anhydrous cupric sulphate of Hampe *loses about seventeen one-hundredths of a per cent of its weight* when subjected to the temperature of the boiling point of mercury; a loss nearly equal to the deficiency which we are seeking to explain. The residual salt may be slowly dissolved in water without the need of very great caution. It gives a perfectly clear solution, which is neutral to methyl orange and does not deposit basic salt even upon indefinite standing. These facts alone show that the decrease in weight was not due to loss of acid, but a much more definite proof of this point is given later.

For electrolysis, the clear solution of the 1.95637 grams of cupric sulphate was transferred to a large platinum crucible. This crucible had been previously coated inside with pure copper, washed with

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\* This is a mean of the results of Hampe and Karsten.

water and alcohol, and dried at  $103^{\circ}$ . The crucible was supported upon a platinum triangle in the interior of a large breaker, and was covered by a watch glass into which was fused the positive electrode. The wires conducting the current into the beaker were of platinum. The whole apparatus was covered with a large watch-glass, which effectually excluded impurity. Several times before the conclusion of the electrolysis the drops adhering to the inner watch-glass were washed back into the crucible by means of apparatus especially adapted for the purpose. After the maintenance for 120 hours of a weak current,\* the electrolysis was interrupted, and every trace of the acid in the crucible was washed as rapidly as was consistent with scrupulous care into a large platinum bottle. The crucible was then washed with pure alcohol, dried at  $103^{\circ}$ , and finally weighed.

	Grams.
Crucible + Cu before electrolysis (Bar. = 767 ; $t^{\circ}$ = $20^{\circ}$ )	= 36.12120
“ + additional Cu after (Bar. = 750 ; $t^{\circ}$ = $20^{\circ}$ )	= 36.90000
Apparent weight of copper	= 0.77880
Correction for change in temperature and pressure	= + .00007
“ to vacuum	= - .00001
True weight of copper in vacuum	= .77886

	Per Cent.
Percentage of copper in $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	= 25.452
“ “ “ $\text{CuSO}_4$ dried at $255^{\circ}$	= 39.744
“ “ “ “ dried at $250^{\circ}$ (Hampe)	= 39.725
“ “ “ “ dried at $365^{\circ}$	= 39.811

Further comment here is unnecessary.

The earlier experiments had already shown approximately the equivalent ratio of sodic carbonate to copper. Accordingly a very little less than the amount of sodic carbonate corresponding to the data above was carefully weighed out from the second sample of this material, and the salt was ignited at a dull red heat until constant in weight.†

	Grams.
Weight crucible + $\text{Na}_2\text{CO}_3$	= 21.60095
“ “ alone	= 20.30260
“ sodic carbonate in air	= 1.29835
“ “ “ in vacuum (Sp. gr. = 2.466)	= 1.29880

\* These Proceedings, XXV. 202.

† See description of sodic carbonate, page 247 of this paper.

The sodic carbonate was dissolved in water and poured into the very dilute solution of sulphuric acid which had been formed by the electrolysis. The lid of the crucible, as well as that vessel itself, was very thoroughly washed with water. On account of the great dilution of the liquid, carbonic anhydride was not at once set free, but upon warming for six or eight hours upon the steam bath it was easily expelled. During this operation the platinum flask was of course suitably covered, a Gooch crucible being found most convenient for this purpose.

When gas evolution had long ceased, the solution was wholly transferred to a large platinum dish, and was evaporated on the steam bath to a volume of about fifty cubic centimeters. The very slight excess of acid was then titrated by means of sodic hydroxide, using methyl orange as an indicator, and was found to require 0.09 cubic centimeter of a decinormal solution for neutralization. The probable error of the end point was not greater than one drop, or one ten-thousandth part of the sodic carbonate present.

	Grams.
Sodic carbonate weighed out	= 1.2988
“ “ added in titration	= 0.0005
“ “ required (in vacuum)	= 1.2993
Cupric sulphate taken ( $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ )	= 3.06006
Copper found in “ “	= .77886

Per cent of  $\text{SO}_4$  in  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  = 38.439

Atomic weight of copper :

$\text{Na}_2\text{CO}_3 : \text{Cu}$  = 106.108 : 63.606

In transferring the sodic sulphate from the evaporating dish to the capacious platinum crucible in which it was to be weighed, the precaution of washing with water which had been thoroughly boiled was absolutely essential to prevent the possibility of subsequent mechanical loss during evaporation. At best, the concentration of a solution in an open crucible over the steam bath is an unsatisfactory operation, and accordingly for the third series a new method was devised. The water left the sodic sulphate very slowly ; but in the end it evaporated so completely that after covering there was a scarcely audible decrepitation on heating the crucible to redness. The pure white sodic sulphate was finally fused at a bright red heat. During this last operation the salt occasionally became tinged with a slightly yellowish hue, due probably to a trace of iron from the platinum vessels ; but the purest specimens remained wholly colorless. The salt lost only one



or two tenths of a milligram during the fusion. A drop of very dilute permanganate solution was not decolorized by the solution of the residual salt, showing that no reduction had taken place. A very small amount of insoluble residue, consisting of the apparently unavoidable impurity in the sodic carbonate together with any iron or copper which might be present, was determined in each case; and the amount was subtracted from the weight of sodic sulphate. Naturally, besides this, it is necessary to subtract the amount of salt corresponding to the *acid* added in titrating back and forth when determining the end point of the acidimetric reaction. This end point had been taken as the average of a number of readings. Below are the data of the experiment under discussion.

	Grams.
Weight of crucible + $\text{Na}_2\text{SO}_4$ (etc.)	= 18.67040
“ “ alone	= 16.92594
Uncorrected weight of $\text{Na}_2\text{SO}_4$	= 1.74446
Subtract weight of salt added in titration	= .00362
“ “ insoluble residue	= .00034
Corrected weight of $\text{Na}_2\text{SO}_4$ in air	= 1.74050
Correction to vacuum (Sp. gr. = 2.631)	= +.00063
Weight $\text{Na}_2\text{SO}_4$ in vacuum	= 1.74113

Per cent of $\text{SO}_4$ in $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	= 38.445
“ “ “ “ found above	= 38.439

Atomic weight of copper (if  $\text{Na}_2\text{SO}_4 = 142.166$ , from table) :

$$\text{Weight } \text{Na}_2\text{SO}_4 : \text{weight Cu} = 142.166 : 63.595.$$

No copper was found in the solution of the sodic sulphate, and a minute trace only in the insoluble residue.

The object of the second experiment of the series was to determine whether the method of weighing cupric sulphate in a tightly covered crucible was an accurate one. The determination was in every respect modelled after the mode of procedure adopted by Hampe, a tightly stoppered weighing-bottle being used to contain the salt. The result sufficiently confirmed the previous experiment. For later experiments a crucible was accordingly used, since the evaporation of sulphuric acid at high temperatures is much more feasible in such an apparatus. A mishap prevented the accurate determination of the acid.

For the third experiment, a much larger amount of material was

used, the method being essentially that of the first experiment. The large crucible of one hundred and fifty cubic centimeters' capacity used for the electrolysis was not previously coated with copper. The end point of the acidimetric determination was taken with both phenol phthalein and methyl orange, the color change with the latter indicator being rather unsatisfactory in the presence of so large an amount of dissolved substance. The amount of insoluble residue found in the sodic sulphate was only 0.0003 gram; it contained no trace of copper. The results showed that little was to be gained by the use of larger quantities of substance, since the unavoidable errors of quantitative work were multiplied nearly in proportion to the quantities of material. Mechanical errors are at the present day inessential compared with the constant ones which complicate so many analyses. It is obvious that a far more accurate result could be obtained from four tenths of a gram of really anhydrous cupric sulphate, than from four hundred grams of a substance still retaining nearly two tenths of a per cent of water.

Adding in the small amount of water which is lost by cupric sulphate between  $255^{\circ}$  and  $365^{\circ}$ , the percentage composition of the crystallized salt, as indicated by the second series of analyses, gives a much more satisfactory total result than before:—

Water lost at $255^{\circ}$	= 35.960
Additional water lost at $365^{\circ}$	= 0.108
Copper	= 25.450
Sulphuric acid radical	= <u>38.436</u>
Total	= 99.954

Although greatly improved, the analysis still leaves much to be desired. Even in materials prepared with the described precautions, traces of impurity were manifest. In the last experiment, where a large amount of material was used, a few minute spots, which might have been arsenic, appeared on the clear surface of the electrolytic copper, and traces of a brownish coloration were observed upon the positive pole. Both of these impurities were so infinitesimal in amount that they could not reasonably have been expected seriously to affect the final result; but the thought that they might be responsible for a part of the remaining deficiency prompted the execution of a still more elaborate series of experiments. The data and results of the second series are appended:—

## ANALYSIS OF CUPRIC SULPHATE.—SECOND SERIES: DATA.

*Weights reduced to Vacuum Standard.*

No. of Experiment.	CuSO <sub>4</sub> ·5H <sub>2</sub> O taken.	CuSO <sub>4</sub> (260°) taken.	CuSO <sub>4</sub> (360°) found.	Metallic Copper found.	Sodic Carbonate required.		Sodic Sulphate found.
					Methyl Orange.	Phenol Phthalein.	
	grams.	grams.	grams.	grams.	grams.	grams.	grams.
4	3.06006	1.9597	1.95637	0.77886	1.2993	....	1.7411
5	2.81840	1.8048	....	0.71740			
6	7.50490	4.8064	4.79826	1.90973	3.1859	3.1865	4.2679

## SECOND SERIES: RESULTS.

No. of Experiment.	Water lost at 260°.	Additional loss at 360°.	Total Per Cent of Water (360°).	Per Cent of Copper.	Per Cent of SO <sub>4</sub> by Na <sub>2</sub> CO <sub>3</sub> (average).	Per Cent of SO <sub>4</sub> by Na <sub>2</sub> SO <sub>4</sub> .
4	35.959	0.109	36.068	25.452	38.439	38.444
5	35.964	....	....	25.454		
6	35.957	0.108	36.065	25.446	38.435	38.424
Averages	35.960	0.108	36.067	25.450	38.437	38.434

## THIRD SERIES.

It is only by gradual approach that very accurate quantitative work may be realized, and the earlier series were absolutely necessary as a training and preparation for the present one. This series had for its object, not only an investigation of the effect of increased refinement, but also a definite proof that the amount of acid present in cupric sulphate was unaffected by the operations involved in the dehydration of the salt. To this end the first sample was not dehydrated at all, the second was heated only to 250°, and the third was exposed to the full heat of 365°, after the addition of sulphuric acid. Since the percentage of acid found in these samples did not vary beyond a reasonable limit of error, the proof is satisfactory.

The additional precautions taken in the preparation of the materials have already been mentioned under appropriate heads. Besides these,

many refinements of manipulation were employed, too numerous to be fully described. For example, phosphorous pentoxide was used as a drying agent in the desiccator, and immediately after the introduction of a hot crucible the air was exhausted with a good air-pump and readmitted through a series of drying tubes. This method of course absolutely prevents the absorption of moisture by the contents of the crucible, while cooling.

Again, in the ninth experiment, the solution of the perfectly neutral sodic sulphate was transferred to a small flask, heated to  $103^{\circ}$ , and evaporated by means of a current of pure dry air. When dry, the sulphate was gently ignited and weighed in the flask, and subsequently fused in a platinum crucible. The flask lost 0.00010 gram during the operations, and the sodic sulphate lost 0.0003 gram upon fusion. With the exception of the small flask, all the apparatus was of platinum. The sodic sulphate formed in the second experiment, and the sodic carbonate required in the third, were not determined.

The last experiment of the series was not of the same grade of refinement with the others. It is only included here because the same preparation of cupric sulphate was used in its execution.

The determination of the sulphuric acid by still another method was the object of this experiment. Baric sulphate was precipitated from a boiling solution of cupric sulphate strongly acidified with hydrochloric acid. After weighing as usual, the perfectly white precipitate was fused with pure sodic carbonate, and the resulting cake thoroughly lixiviated with boiling water and dilute sodic carbonate solution. In the filtrate, the chlorine, which had been originally present as baric chloride occluded in the sulphate, was determined in the usual manner. Traces of baric sulphate and argentic chloride must have been dissolved in the wash water, but these errors tend to counterbalance one another, and hence no correction was made for them. Finally, the weight of baric chloride, calculated from the amount of chlorine found, was subtracted from the weight of baric sulphate; and from the corrected weight thus obtained the percentage of sulphuric acid in cupric sulphate was calculated. The astounding agreement of this experiment with the others may be nothing more than accident. In any case, the uncertainty of the atomic weight of barium, and the very unsatisfactory nature of baric sulphate, combine to make a repetition of the experiment of little value for the present purpose; but the method seems to be of value, and will form a subject of future investigation in this Laboratory. It is well known that baric sulphate has

great power of occluding many salts, but few experimenters seem to have realized that the occlusion of most metallic sulphates tends to *decrease* the amount of precipitate obtained. This fact was recognized by Professor Jannasch and the writer\* in 1889, and would influence the controversy between Ostwald† and Krüss.‡ The occlusion of baric chloride of course increases the amount of precipitate when sulphuric acid is to be determined, and diminishes it when barium is to be determined. With care this last error may be reduced to a very small amount, but it is doubtful if it has ever been wholly avoided. A trace only of copper was found in the precipitate obtained in the experiment described above, showing that cupric chloride is not occluded to any essential extent.

In spite of the fact that the important analyses of the third series were far more carefully performed than those of the second, the result was no more satisfactory than before. It was therefore apparent that a point had been reached beyond which further refinement was unavailing, and that the reason of the discrepancy must be sought, not in accidental or variable impurity, but rather in some property inherent in the purest cupric sulphate.

## ANALYSIS OF CUPRIC SULPHATE.—THIRD SERIES: DATA.

*Weights reduced to Vacuum Standard.*

No. of Experiment.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ taken.	$\text{CuSO}_4$ found.	Metallic Cu found.	$\text{Na}_2\text{CO}_3$ found by Methyl Orange.	$\text{Na}_2\text{CO}_3$ found by Phenol Phthalein.	Sodic Sulphate found.
7	grams. 2.88307	grams. .... at $260^\circ$	grams. 0.73380	grams. 1.2242	grams. 1.22435	grams. 1.63994
8	3.62913	2.32373 at $370^\circ \pm$	0.92344	1.5407	1.54080	
9	5.81352	3.71680	1.47926	....	....	3.30658
	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ taken.		Baric Sulphate found (uncor.).	Argentie Chloride found.	Baric Chloride calculated.	Baric Sulphate corrected.
10	grams. 3.1902		grams. 2.9967	grams. 0.0284	grams. 0.0206	grams. 2.9761

\* J. für prakt. Chemie, XXXIX. 321 (1889).

† Lehrbuch der Allgem. Chem., I. 53.

‡ Annalen, CCLXII. 40.

## THIRD SERIES: RESULTS.

No. of Experiment.	Water lost at 260°.	Water lost at 370° $\pm$ .	Copper found.	SO <sub>4</sub> found from Na <sub>2</sub> CO <sub>3</sub> (average).	SO <sub>4</sub> found from Na <sub>2</sub> SO <sub>4</sub> .
7	....	....	25.452	38.443	38.433
8	35.970	....	25.446	38.435	
9	....	36.067	25.445	....	38.431
10					From Baric Sulphate. 38.434
Average	35.970	36.067	25.448	38.439	38.433

## PERCENTAGE COMPOSITION OF CUPRIC SULPHATE.

	Second Series.	Third Series.	Theoretical.	
			Cu = 63.60.	Cu = 63.33.
Water	36.068	36.067	36.0695	36.109
Copper	25.450	25.448	25.4665	25.385
SO <sub>4</sub>	38.436	38.436	38.464	38.506
	99.954	99.951	100.000	100.000

*The Cause of the Deficiency.*

It was by no means easy to trace the cause of the disappearance of less than one two-thousandth part of the material to its true source.

The notable agreement between the percentages of water given in the first three columns of figures immediately above of course suggested the possibility of a loss of copper and sulphuric acid during the electrolysis; and it became an important matter to test the point.

Accordingly weighed portions of a dilute solution of pure sulphuric acid were estimated with weighed amounts of sodic carbonate. Other portions of the same solution, weighed alternately with the previous ones, were then evaporated over the water bath with small amounts

of cupric nitrate and successive additions of water. The cupric sulphate formed by this treatment was wholly decomposed by electrolysis, and the resulting sulphuric acid was determined exactly in the usual manner. The comparison of the acid solution before and after electrolysis is capable of showing at once whether any sulphuric acid was mechanically or chemically lost during the process. If any nitric acid had been held by the sulphuric acid in the second case, it could not have escaped decomposition during the electrolysis.

Following are the results:—

STRENGTH OF  $\text{H}_2\text{SO}_4$  BEFORE ELECTROLYSIS.

*Weights reduced to Vacuum.*

Number of Experiment.	Solution taken.	$\text{Na}_2\text{CO}_3$ required.	$\text{Na}_2\text{CO}_3$ for 10,000 grams Solution.
11	grams. 5.5932	grams. 1.0175	grams. 1.81917
12	11.4175	2.0768	1.81896
Average . . .			1.81906

STRENGTH OF  $\text{H}_2\text{SO}_4$  AFTER ELECTROLYSIS.

*Weights reduced to Vacuum.*

Number of Experiment.	Solution taken.	$\text{Na}_2\text{CO}_3$ required.	$\text{Na}_2\text{CO}_3$ for 10,000 grams Solution.
13	grams. 16.8214	grams. 3.0592	grams. 1.81865
14	5.5612	1.0115	1.81886
Average . . .			1.81876

Difference between averages . . . 0.0003.

Known mishaps tended to make the first experiments of each of the two groups respectively too high and too low. It is seen that the second experiments gave nearly identical results. Considering the increased transference and manipulation involved in the second group,

the conclusion seems to be warranted that little if any sulphuric acid is lost during electrolysis.

In order to prove like relations with regard to copper a similar method was adopted. Weighed amounts of electrolytic copper were dissolved in pure nitric acid in a flask provided with bulb tubes for the condensation of spray. The cupric nitrate was then evaporated with an excess of sulphuric acid upon the water bath, and the cupric sulphate was electrolyzed as usual.

#### ELECTROLYSIS OF COPPER.

Number of Experiment.	Copper taken.	Copper found.	Loss of Metal.
	grams.	grams.	grams.
15	1.24156	1.24139	0.00017
16	1.00613	1.00600	0.00013

Here again, the manipulation was so much more elaborate than in a simple electrolysis that it is difficult to decide where the slight loss took place. In another experiment (No. 17) both copper and sulphuric acid were weighed before and afterward, but the experimental operations were so doubly involved that the determination was of very doubtful value. The result was not materially different from the others, however. The significant portions of the data are given in another place.\*

In the course of these experiments it was found that a compact and brilliant copper film may be safely washed by decantation if sulphuric acid alone is present. Indeed, during most of the preceding determinations this method was adopted to insure complete collection of the acid, and in only one case (Experiment 7) was as much as one twentieth of a milligram of copper found in the filtrate. In this case that amount was added to the larger quantity, and the sum is given in the table. Potassic ferrocyanide was the reagent used in the colorimetric tests.

Assuming the deficiency of copper and acid as found above to represent a real loss during electrolysis, the composition of cupric sulphate would be :—



	Uncorrected.	Corrected.
Water . . . . .	36.067	36.067
Copper . . . . .	25.449	25.452
SO <sub>4</sub> . . . . .	38.435	38.442
	99.951	99.961

That is to say, an undoubtedly excessive value for this correction would account for only one fifth of the deficiency for which explanation was sought. The correction is at best very doubtful, and it is not applied in the final calculation of the atomic weight. Its application would make no essential difference in the final result, but would render the individual variations much less marked.

The only probable interpretation of the deficiency now lay in the assumption that cupric sulphate still held a volatile impurity at 360°. Such an amount of any non-volatile foreign substance would have increased the weight of sodic sulphate found at the conclusion of the analysis by about eight one-hundredths of one per cent, an amount entirely too large to escape detection. Besides, such a source of error had already been shown to be unlikely.

After it had been experimentally proved that cupric sulphate had no tendency to hold ammoniac sulphate at 370°, the hypothesis of the occlusion of a small amount of water became the last resource. At first sight it seems improbable that any material could hold appreciable quantities of water in the presence of sulphuric acid when so strongly heated. But it must be remembered that at this temperature the acid is dissociated, and water is actually present in the vapor. It was hoped that sulphur trioxide might be more efficient as a dehydrating agent, but a single experiment (No. 18) showed that cupric sulphate possessed more affinity for water even at 300° than did the sulphur trioxide. 2.3787 grams (in vacuum) of cupric sulphate lost 0.8554 gram in weight on heating to about 300° in a glass tube under a current of dry air. Upon continuing the application of heat in air charged with sulphuric anhydride from Nordhausen acid, no essential change in weight was observed. The apparatus was somewhat complicated in order to avoid rubber connections, but a description of it is superfluous. The total loss was 35.962 per cent of the weight taken.

Experiments showed that between  $360^{\circ}$  and  $400^{\circ}$  cupric sulphate does not essentially lose in weight. For example (No. 19 or 23), 1.28563 grams of the substance dried at the former temperature weighed 1.28558 grams after heating for ten hours at  $400^{\circ}$ . At the temperature of dull redness the salt slowly decomposes.

If the loss of weight during this decomposition could be compared with the deficiency of sulphuric acid in the residue, it is evident that an indirect means would be at hand for the detection of a possible simultaneous loss of water. Such a circuitous road seemed to be the only one open to the present search.

In the series of experiments tabulated below, pure cupric sulphate was heated in the usual manner to  $250^{\circ}$ , and then after the addition of sulphuric acid to  $400^{\circ}$ , until the salt became constant in weight. The heat was then increased to dull redness, and after cooling the loss of weight was determined. Upon solution of the residue in water a small amount of basic salt was naturally deposited. Since the filtrate was apparently quite normal, it is evident that the amount of sulphuric acid necessary exactly to dissolve this precipitate must have been equivalent to the anhydride driven off.

After standing a considerable time, the basic salt was carefully filtered off and a measured amount of twentieth normal acid was used for its solution. The crucible used for the ignition was also washed with a measured quantity of acid. The clear solutions were all combined, and the excess of acid was determined by sodic hydroxide and methyl orange. Since the loss of weight upon ignition was noticeably more than the amount of anhydride corresponding to the quantity of sulphuric acid used to dissolve the basic salt, something beside sulphur trioxide must have been expelled by the heat.

The last column of the table gives the difference between the loss of weight of the cupric sulphate and the amount of sulphuric anhydride required to dissolve the basic salt, expressed in percentage of the original crystallized compound. This difference probably represents a small amount of water held even at  $400^{\circ}$ . The results showed a very noticeable variation, and at first sight appeared somewhat unsatisfactory. The first two experiments agreed well with each other, and were apparently very trustworthy. In the third, on the other hand, the amount of basic salt was so large as greatly to interfere with the accuracy of the result. In Experiment 23 the loss of weight upon ignition was so very large, amounting to about three per cent of the anhydrous sulphate, that the experiment was rejected. After such a failure, it was natural that the next sample should not have

been heated enough. This result is hence probably too low. The last experiment was more carefully regulated, and is more trustworthy. In this case the cupric sulphate was heated for an hour at very dull redness.

## ACTION OF HEAT UPON CUPRIC SULPHATE.

*Weights reduced to Vacuum.*

Number of Experiment.	Weight of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . grams.	Weight of $\text{CuSO}_4$ [260°]. grams.	Weight of $\text{CuSO}_4$ [400°]. grams.	Weight after ignition at dull Redness. grams.	Loss between 400° and Redness. milli-grams.	$\frac{1}{20}$ normal $\text{H}_2\text{SO}_4$ required for Basic Salt.		Per Cent of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ unaccounted for.
						Uncorrected.	Corrected.*	
20	—	1.5822	1.57945	1.57325	6.2	2.65	2.55*	0.044
21	2.71828	1.7413	1.73836	1.73130	7.06	2.95	2.85*	0.050
22	4.7325	—	3.0258	2.9928	33.0	16.36	[15.86*?]	[0.030?]
23	2.01084	1.2880	1.2856	1.2504	35.2	—	—	—
24	7.211	—	4.6075	4.6055	2.0	0.33	0.32*	0.019
25	3.979	—	2.5443	2.5403	4.0	0.93	0.90*	0.055
Total Average . . . . .								0.040
Average omitting 22 . . . . .								0.042

The filtrates from the precipitates of basic salt did not deposit any further solid upon long standing. That from the last determination was rendered very distinctly acid to methyl orange by the addition of a milligram of sulphuric acid, in spite of the difficulty in detecting the color-change in the presence of the blue cupric sulphate. These tests indicate that the filtrate was wholly normal.

In order to test still more definitely the accuracy of the method, the following mode of procedure was devised. To neutral solutions of cupric sulphate—prepared either from the purest crystals or by long standing after the neutralization of the trace of acid in ordinary “chemically pure” material—were added small measured amounts of a standard sodic hydroxide solution. After a time, the precipitate was filtered off and dissolved in standard sulphuric acid, exactly as if it had been obtained by the expulsion of the acid through heat.

\* See page 266, Experiments 26–37.

## TEST OF METHOD.

*Precipitation and Solution of Basic Cupric Sulphate.*

Number of Experiment.	Concentration of Solution.	Time between Precipitation and Filtration.	Twentieth normal NaOH used.	Twentieth normal $H_2SO_4$ used.	Factor $\frac{c. c. NaOH}{c. c. H_2SO_4}$
26	Strong.	10 minutes.	cub. centim. 3.00	cub. centim. 2.85	1.05
27	Strong.	90 minutes.	3.00	2.94	1.02
28	Medium.	15 hours.	3.00	3.14	.95
29	Dilute.	1 hour.	6.00	6.24	.96
30	"	90 minutes.	6.00	6.27	.95
31	"	" "	3.00	3.12	.96
32	"	" "	3.00	3.14	.95
33	"	" "	3.00	3.03	.99
Average of Experiments 28-33 . . . . .					0.96

It is hence evident that from dilute solutions the basic salt is wholly precipitated in a comparatively short time. Even under the worst conditions no deficiency approaching that noticed in Experiment 25 was observed. Another series (Experiments 34-37), made in very dilute solutions without filtering, gave values for the factor which respectively equalled 0.97, 0.98, 0.95, and 0.98. The average is 0.97, not seriously different from that found above. The first value of the factor was used in correcting the results of Experiments 20-25. The correction involved is extremely slight except in Experiment 22, where the application of the full value of the factor to a very large quantity is of doubtful advisability. Hence it is better to omit this experiment from the final average.

One contingency alone is not provided for by these test experiments that is to say, the formation of a cuprous compound and its solution in the cupric salt. The formation of a cuprous salt by gentle ignition of cupric sulphate in the air is far from probable; but for fear that such a reaction had taken place, the solution of the cupric sulphate was usually exposed to the air from twelve to twenty-four hours before filtration. The fact that exposure to the air for a long time after

filtration caused no further formation of precipitate is a satisfactory proof that no cuprous salt remained in solution, even if it had been formed in the first place.

The outcome of all these more or less indirect experiments points to the conclusion that cupric sulphate retains about 0.12 per cent of its water of crystallization, even when heated to  $400^{\circ}$  C. This last trace of water is given off only at a temperature at which the cupric sulphate itself begins to decompose. It must be admitted that the evidence upon the point is not absolutely certain, but there is no doubt of its great probability. Upon such a matter as this it is difficult to see how more definite results could have been procured.

*Total Percentage Composition of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ .*

	Per Cent.
Water lost at $360^{\circ} - 400^{\circ}$	= 36.067
“ “ between $400^{\circ}$ and redness	= 0.042
Copper, average	= 25.449
$\text{SO}_4$	= 38.436
Total	= 99.994

If the amounts of copper and sulphuric acid supposed to be lost during the electrolysis are added, the total becomes 100.004.

Either of these total results is now accurate within the limits of error of ordinary analysis. But it will be seen that the total percentage of crystal water indicated by the analyses is much too large as compared with the sulphuric acid, which is our only certain standard of reference. This excess of water must have been occluded in the original crystals, which were not very finely powdered. Accordingly two specimens of the purest cupric sulphate were much more finely pulverized, and their loss of weight at  $400^{\circ}$  was then found to be 36.057 (average of Experiments 21 and 23) instead of 36.067 per cent. Mr. H. M. Richards kindly measured many diameters in the two powders, and found that the particles of the coarser powder approximated one tenth of a millimeter, while those of the finer were less than one hundredth. Since more than half an hour's continuous powdering, at the very slow rate adopted to prevent warmth from friction, had been necessary to reduce a small amount of material to the finer state, it was concluded to abandon the attempt at obtaining cupric sulphate free from occluded water.

It must be remembered that the salt had been very slowly crystallized by the evaporation of the solution, and of course had had every

opportunity to imprison traces of the mother liquor. Crystallization from hot solutions could not be adopted because of the risk of the formation of basic salt.\* But even if the true amount of the water of crystallization could have been determined, it would have been of little present use for the determination of the atomic weight of copper, because of the uncertainty in its molecular weight. It is hoped that an investigation of the quantitative relations of water in other compounds may be in progress during the coming year at this Laboratory.

*The Atomic Weight of Sulphur.*

It is seen that the ratio between the weights of sodic carbonate and sodic sulphate found in each analysis of cupric sulphate forms a valuable check upon the purity of the first substance. Conversely, if we assume the purity of each of the substances and the molecular weight of one of them, we obtain data for calculating the molecular weight of the other. Since sulphur is probably the least definitely determined of the elements involved, the figures may be used with advantage for the calculation of its atomic weight.

MOLECULAR WEIGHT OF SODIC SULPHATE.

*Weights reduced to Vacuum.*

No. of Experiment.	Source of Acid.	Na <sub>2</sub> CO <sub>3</sub> taken.	Indicator.	Na <sub>2</sub> SO <sub>4</sub> found.	Molecular Weight Na <sub>2</sub> SO <sub>4</sub> if Na <sub>2</sub> CO <sub>3</sub> = 106.108.
4	Electrolysis	grams. 1.29930	M. O.	grams. 1.74113	142.189
6	"	3.18620	Av.	4.26790	142.131
11	Distillation	1.01750	M. O.	1.36330	142.169
12	"	2.07680	M. O.	2.78260	142.169
7	Electrolysis	1.22427	Av.	1.63994	142.133
17	Distillation	1.77953	Phth.	2.38465	142.189
17	Electrolysis	2.04412	Phth.	2.73920	142.189
38	Distillation	3.06140	Phth.	4.10220	142.180
Average Molecular Weight of Na <sub>2</sub> SO <sub>4</sub> . . . . .					142.169
Average omitting Experiments 4, 6, and 7, which are less reliable than the others . . . . .					142.181

\* Hampe, *loc. cit.*

The first column of this table indicates the original number of the experiment. The data of Experiments 17 and 38 are given for the first time. The second column shows the source of the acid. The third column gives the weights of sodic carbonate taken; while in the fourth are recorded the indicators used in determining these weights, the abbreviations standing for methyl orange, phenol phthalein, or the average of the two. The last two columns contain respectively the weight in grams and the molecular weight of the sodic sulphate. Since half of the results were obtained with methyl orange, it is unnecessary to correct the result for the trace of impurity in the sodic carbonate.

Subtracting from the averages the quantity  $\text{Na}_2\text{O}_4 = 110.106$  we obtain two values for the atomic weight of sulphur:—

From the first average,	S = 32.063
“ second average,	S = 32.075
Usually accepted value,	S = 32.06

A large alteration in the assumed atomic weight of sodium would of course make very little difference in the result, while an alteration of  $\frac{1}{1000}$  of its value in the atomic weight of carbon changes the atomic weight of sulphur by only about the twentieth of one per cent. Although it is certain that the results are hardly capable of deciding the present uncertainty in the atomic weight of sulphur, the outcome of the comparison is nevertheless an interesting check upon the work previously described.

The check just mentioned proves that the sodic carbonate contained the normal amount of carbon dioxide, but does not prove the absence of a very small amount of neutral impurity from the salt. Such impurity would have but a slight effect upon the ratio of the weights of the two compounds. It is true that this effect would be to diminish instead of to increase the observed atomic weight of sulphur; but it was thought advantageous to attempt the comparison of the sodic carbonate with some salt having a very different equivalent weight, in order to obtain more light upon this point. Accordingly the material to be investigated was converted with suitable precautions into sodic bromide. In Experiment 39, 1.2198 grams (in vacuum) of sodic carbonate yielded 2.3685 grams (in vacuum) of the bromide; or  $2 \text{ NaBr} : \text{Na}_2\text{CO}_3 = 206.022 : 106.103$ . Upon its face the result was very satisfactory, but the great hygroscopic power of sodic bromide and various other complications afforded a wide possibility of error; hence the experiment was not repeated. To be of value, any such

determination must be made the subject of an especial investigation ; and for this, with so remote a purpose as the present one, time was wanting.

*The Atomic Weight of Copper.*

The calculation of the atomic weight of copper from the amount of metal contained in cupric sulphate which has been dried at 250–270° gives the value 63.35. This result sufficiently approaches Hampe's (63.32) to show the identity of the materials used. But it has been proved that such cupric sulphate still contains a comparatively large amount of water ; and this fact renders useless the careful analyses made in 1874. The effect of the correction is considered in a following paragraph.

Besides this method of calculation "from difference," the data which have been given afford twelve other ratios for the computation of the atomic weight of copper. Six of these ratios are useless because of the known error in the crystal water ; namely,  $5 \text{ H}_2\text{O} : \text{Cu}$  ; —  $\text{SO}_4 \cdot 5 \text{ H}_2\text{O} : \text{Cu}$  ; —  $5 \text{ H}_2\text{O} : \text{CuSO}_4$  ; —  $\text{Na}_2\text{CO}_3 : \text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$  ; —  $\text{Na}_2\text{SO}_4 : \text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$  ; — and  $\text{BaSO}_4 : \text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$ . Three of these last ratios give values which are much too low, and the other three give values which are much too high, as would naturally be expected. The mean is curiously near to the true value, but need not be further discussed. Neglecting these results because of the known constant error which vitiates them, there still exist seven ratios which do not involve the uncertain amount of the water of crystallization.

I. From calculation based upon the results tabulated on page 267 anhydrous cupric sulphate is seen to contain certainly over 39.807 per cent of copper, and very probably as much as 39.832 per cent. The first number gives 63.53 as the atomic weight of copper, and this value must be regarded as the lowest possible limit. The second much more probable figure, which takes into account the water held by cupric sulphate at 400°, gives the proportion :

$$(\text{CuSO}_4 - \text{Cu}) : \text{Cu} = (100.000 - 39.832) : 39.832 = 96.06 : \mathbf{63.593}.$$

II. From Experiments 4, 6, 7, and 8 it is found that 7.2501 grams of sodic carbonate correspond to 4.34583 grams of copper when methyl orange is used as an indicator ; and from Experiments 6, 7, and 8 it is found that 5.95165 grams of sodic carbonate correspond to 3.56697 grams of copper when phenol phthalein is used as an indicator. It has been shown that the impurities of the sodic carbonate



probably rendered the latter quantity of the salt about 0.007 per cent too high; hence the true weight should have been 5.95123. The correction is so small that it has not heretofore been applied.

From these values we obtain the proportions :

$$\begin{aligned}\text{Na}_2\text{CO}_3 : \text{Cu} &= 7.25010 : 4.34583 = 106.108 : 63.603 \\ &= 5.95123 : 3.56697 = 106.108 : 63.597 \\ \text{Average} & \qquad \qquad \qquad \mathbf{63.600}\end{aligned}$$

The highest individual result was 63.604, the lowest 63.592, when entirely uncorrected.

III. From Experiments 4, 6, 7, and 9 it is apparent that 10.95552 grams of sodic sulphate are equivalent to 4.90165 grams of electrolytic copper. Hence :

$$\begin{aligned}\text{Na}_2\text{SO}_4 : \text{Cu} &= 10.9555 : 4.90165 = 142.166 : \mathbf{63.607}.\end{aligned}$$

Highest value	63.614
Lowest "	63.595

The last determination (Experiment 9) is by far the most trustworthy. The value deduced from it is 63.600.

IV. From Experiments 4 and 6 it is evident that 4.4855 grams of sodic carbonate (average) are equivalent to 6.75463 grams of cupric sulphate which has been dried at 360°. But it is reasonably certain that this cupric sulphate still contained sixty-six hundred-thousandths of its weight of water. Making the appropriate correction we have :

$$\begin{aligned}\text{Na}_2\text{CO}_3 : \text{CuSO}_4 &= 4.4855 : (6.7546 - .0044 = 6.7502) \\ &= 106.108 : 159.681\end{aligned}$$

Highest value	159.703
Lowest "	159.673

Subtracting  $\text{SO}_4 = 96.060$ , the average value  $\text{Cu} = \mathbf{63.621}$  is obtained.

V. In the same way, from Experiments 4, 6, and 9, 9.31558 grams of sodic sulphate are seen to correspond with  $10.4715 - 0.0069 = 10.4646$  grams of really anhydrous cupric sulphate. Hence :

$$\begin{aligned}\text{Na}_2\text{SO}_4 : \text{CuSO}_4 &= 9.3156 : 10.4646 = 142.166 : 159.701\end{aligned}$$

Highest	= 159.73
Lowest	= 159.65

From the average,  $\text{Cu} = \mathbf{63.641}$ . This result has a very large probable error, in the chemical as well as in the mathematical sense.

VI. and VII. Only one experiment was made with baric sulphate, but the result is appended for the sake of completeness. From No. 10 it is seen that 100.000 parts of crystallized cupric sulphate are equivalent to 93.289 parts of baric sulphate. But the same amount of the same specimen of the salt had been shown to contain 25.448 parts of copper and 36.109 parts of water. (See pages 260 and 267.) From these data:—

$$\text{VI. BaSO}_4 : \text{Cu} = 93.289 : 25.448 = 233.16 : \mathbf{63.603}$$

$$\text{VII. BaSO}_4 : \text{CuSO}_4 = 93.289 : 63.891 = 233.16 : 159.685$$

From the last value  $\text{Cu} = \mathbf{63.625}$ . The atomic weight of barium probably lies between 137.0 and 137.2; the mean value is assumed above. The corresponding variations of the atomic weight of copper would be from 63.57 to 63.63 with the first ratio, and from 63.54 to 63.69 with the second.

The results of the seven ratios dependent upon the analysis of cupric sulphate are collected in the following table.

THE ATOMIC WEIGHT OF COPPER.

	Ratio.	Lowest.	Highest.	Experimental Mean.
I.	$(\text{CuSO}_4 - \text{Cu}) : \text{Cu}$	[63.53]	[63.62]	63.593
II.	$\text{Na}_2\text{CO}_3 : \text{Cu}$	63.592	63.604	63.600
III.	$\text{Na}_2\text{SO}_4 : \text{Cu}$	63.59	63.61	63.607
IV.	$\text{Na}_2\text{CO}_3 : \text{CuSO}_4$	63.61	63.64	63.621
V.	$\text{Na}_2\text{SO}_4 : \text{CuSO}_4$	63.59	63.67	63.641
VI.	$\text{BaSO}_4 : \text{Cu}$	[63.57]	[63.63]	63.603
VII.	$\text{BaSO}_4 : \text{CuSO}_4$	[63.54]	[63.69]	63.625
Average . . . . .				63.612
Average, omitting V. and VII. for obvious reasons . .				63.605

The correction of the experimental mean, in each case, for the amount of copper and sulphuric acid lost during electrolysis, diminishes the variations noticeable above to a remarkable degree. But since the validity of this correction is doubtful, and since its applica-

tion scarcely influences the two most important results (II. and III.), the figures have been allowed to stand uncorrected. The final average would have remained essentially the same. The highest and lowest values given in this table are in several cases much more seriously in error than the actual experimental results. The reasons for this widening of the limits will be sufficiently understood through a careful perusal of the matter which immediately precedes the table.

Changes in the atomic weights of the elements used as standards of reference of course cause slight changes in the corresponding atomic weights of copper. Sulphur enters into a larger number of the ratios than any other element, excepting of course oxygen and copper; but a reasonable change in its assumed atomic weight, while slightly affecting individual results, has no effect upon either of the averages. Carbon and sodium are both determined with a high degree of accuracy, and oxygen is our standard of reference. A fuller discussion of these results will be found in the concluding summary.

## II. SYNTHESIS OF CUPRIC SULPHATE.

Parallel with the experiments which have just been described was commenced a series of syntheses of cupric sulphate. It was hoped that the results might furnish a valuable confirmation to the conclusions based upon the analytical work, but the outcome of the series was very disappointing.

The method of experiment was as follows. A weighed amount of pure electrolytic copper,\* which had been ignited in hydrogen, was dissolved in the purest nitric acid in a platinum flask provided with bulb tubes for the condensation of spray. A slight excess of pure sulphuric acid was then added, and the whole was evaporated to small bulk in a platinum dish. After transferring to a small crucible enclosed in a larger one, the remaining solution was evaporated to dryness on the steam bath; and the residue was gradually raised to a temperature of 400°. After some time the crucible was quickly covered, placed in a phosphoric oxide desiccator, and allowed to cool in a vacuum. Air having been admitted through suitable drying tubes, the crucible was quickly weighed. The product of the experiment soon reached constant weight upon reheating, but it was invariably found to contain a very perceptible amount of imprisoned sulphuric acid, which rendered its solution strongly acid to methyl orange. It is evident from the preceding section that this impurity is

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\* For mode of preparation, see these Proceedings, XXV. 199, 206.  
VOL. XXVI. (N. S. XVIII.) 18

not retained when pure sulphuric acid is added to powdered cupric sulphate which has already been nearly dehydrated, but only when the salt is crystallized from strongly acid solutions. This fact rendered the present experiments useless for their original purpose. The results of the two determinations show how insidious constant error may be, if not guarded against by check experiments.

#### SYNTHESIS OF CUPRIC SULPHATE FROM METALLIC COPPER.

*Weights reduced to Vacuum.\**

Number of Experiment.	Metallic Copper taken.	Cupric Sulphate found.	Per Cent of Copper in Cupric Sulphate.
40	grams. 0.67720	grams. 1.7021	39.786
41	1.00613	2.5292	39.781
Average . . . . .			39.784
From Analysis of Cupric Sulphate dried at 400° . .			39.807

In order to show that the large difference between these two averages was due solely to the occlusion of sulphuric acid, the following experiment (No. 42) was made. 3.1227 grams (in vacuum) of the purest crystallized cupric sulphate were dried at 400°, the residue weighing 1.9963 grams. The nearly anhydrous salt was then carefully dissolved in water, and after the addition of small quantities of nitric and sulphuric acids it was evaporated and ignited at a temperature even somewhat higher than before. A gain of 0.0013 gram was apparent, very nearly corresponding to the difference noted above. The acids, tested immediately afterwards, left no weighable residue upon evaporation.

While it was apparent that these experiments were useless for their original purpose, it was hoped that their comparison with similar syntheses from cupric oxide might furnish valuable indirect evidence with regard to the quantitative relations of the latter important substance. The hope was not in vain.

The cupric oxide used as the basis of the three following experiments was prepared essentially in the manner described in these Proceedings, Volume XXV., page 199. The three experiments represent

\* Specific gravity of Cu = 8.95; of CuSO<sub>4</sub> (Hampe and Karsten) = 3.61.

as many different preparations, in making which various different precautions were observed; but in a paper already far too prolix the omission of these minor points will be well pardoned. The cupric oxide was ignited to constant weight at a dull red heat in a double crucible, and cooled in a vacuum as usual. The outside crucible was of platinum in the second and third experiments, and in these cases the inner crucible was observed to have gained noticeably in weight during the ignition. The last weight was adopted, for obvious reasons. In the first and last cases the solution of the oxide was conducted in the crucible, without transferring, while in the second experiment the cupric oxide was dissolved in the platinum flask with bulb tubes. In each case both nitric and sulphuric acids were added, that the conditions might be similar to those of the preceding syntheses. The cupric sulphate used by Baubigny in his analyses was prepared in a somewhat similar way, and hence in this respect his result is comparable with these.

## SYNTHESIS OF CUPRIC SULPHATE FROM CUPRIC OXIDE.

*Weights reduced to Vacuum.\**

Number of Experiment.	Cupric Oxide taken.	Cupric Sulphate found.	Per Cent Cupric Oxide in Cupric Sulphate.
	grams.	grams.	
43	1.0084	2.0235	49.835
44	2.7292	5.4770	49.830
45	1.0144	2.0350	49.848
Average . . . . .			49.838
Theory if Cu = 63.6 : . . . . .			49.856
" " = 63.34 . . . . .			49.774
Baubigny's result . . . . .			49.815

The comparatively close agreement between the average and the theory is solely due to an elimination of opposite errors. This fact will be more evident in the following section.

In order to show that no material was mechanically lost during the syntheses, the last sample of cupric sulphate from each of the two series was electrolyzed. The result of one of these electrolyses has

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\* Specific gravity of CuO = 6.3; of CuSO<sub>4</sub> = 3.61.

already been given in Experiment 16; the other yielded 0.8096 gram of metal from 2.0350 grams of the sulphate, or 39.78 per cent of copper.

It is evident that impure cupric sulphate prepared in this manner contains about 39.784 per cent of copper and about 49.838 per cent of ordinary cupric oxide. That is to say, 39.784 parts of copper correspond to 10.054 parts of the remainder of cupric oxide. Assuming this remainder to consist solely of oxygen, the atomic weight of copper would be 63.312. But upon comparing the quantity 10.054 with the quantity of sulphuric anhydride found by difference, 50.162, it is evident that a grave error exists in the former figure. This error becomes only more apparent when allowance is made for the occluded acid.

These inferences are based upon data of somewhat uncertain accuracy, it is true; but the error is nevertheless so large as to be apparent even to cruder analysis than this. The full explanation of the results, as well as of the variation exhibited by Baubigny's analysis, must be deferred to the next section. The doubts raised by the data under discussion formed a useful introduction to the study of cupric oxide.

### III. THE ANALYSIS OF CUPRIC OXIDE.

Deprived of the support of the results from cupric sulphate, Hampe's oxide determinations possess little more weight than those of any other experimenter. It will be remembered that the values of the atomic weight of copper deduced from this source have varied from 63.1 to 63.5. Such a fluctuation alone, without the confirmatory evidence which has just been given, is sufficient to cause the suspicion of an undiscovered error in cupric oxide.

With the hope of detecting the possible error, a number of analyses of the substance were made under varying conditions and with different samples of material. No difficulty was found in obtaining results varying as widely as those cited above. Part of the cause of this variation was traced to differences in the preparation, and part to differences in the temperature and tension of the surrounding air employed in ignition.\* Cupric oxide ignited to constant weight at a very dull red heat lost a very perceptible amount of material upon

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\* Compare Bailey and Hopkins, *J. Ch. Soc. Trans.*, 1890, p. 269. Also Schutzenberger, quoted in *Am. J. Sc.*, [3], XXVI. 65.

heating to the highest temperatures which hard glass would bear. On the other hand, copper reduced by hydrogen at the lowest possible temperatures is well known to lose in weight on heating to bright redness. Some of Erdmann and Marchand's experiments\* show that the exhaustion of the tube at the time of weighing makes very little if any variation in the weight of the materials; but from others,† as well as from the fiftieth experiment below, it would appear that exhaustion at the time of ignition introduces a somewhat more serious correction. In this last case the apparatus was necessarily rather complicated, to admit of the ignition and weighing of the copper and its oxide in a Sprengel vacuum, but the full description of the contrivance would demand more space than it is worth. In the four preceding experiments Hampe's method was carefully followed.

The mode of preparation of the cupric oxide was essentially that recommended by Hampe, and described in these Proceedings, Volume XXV., page 199. In some cases the basic nitrate was not washed with water before ignition, and in other cases it was thus washed. In general, none but platinum vessels were used. Various slight unimportant modifications were introduced, which need not find a place here. The essential conditions to be borne in mind are the invariable use of the nitrate as the source of the oxide, and the variable temperatures employed in the ignition.

## ANALYSIS OF CUPRIC OXIDE.

*Weights reduced to Vacuum Standard.*

No. of Exp't.	CuO dull redness 550°±	CuO 750°?	Cu found 400°±.	Cu found 550°±.	Cu found 750°?	Atomic Weight of Copper O : Cu = 16 : x.
	grams.	grams.	grams.	grams.	grams.	
46	2.08491	—	—	1.66405	—	63.26
47	1.11936	1.11851	—	0.89355	—	63.29 to 63.53
48	1.06300	1.06253	[0.8490]	—	0.84831	63.23 to [63.62]
49	1.91703	1.91656	—	—	1.5298	63.20 to 63.29
50	2.62410	Ignited	in vacuum	2.0956	—	63.44
[General Average . . . . .]						63.37]

\* *Loc. cit.* (see p. 241).

† J. prakt. Chem., XXVI. 461.

The average of results so heterogenous in nature can naturally have no important meaning, but it is interesting to note the approximation to the old value of the atomic weight. The high value given in Experiment 48 is manifestly only a compensation of errors. From Experiments 48 and 49, the only two in which both materials were ignited at a bright red heat, 2.97909 grams of cupric oxide yielded 2.37811 grams of metallic copper. Computing from these data the atomic weight of copper, we obtain the value 63.313, which is comparable with the result 63.312 obtained indirectly through the synthesis of the sulphate as well as with the number 63.346 fixed upon by Hampe. The absolute identity of the first two figures must be attributed to chance, since the agreement of the individual results was not perfect.

These results again pointed to the existence of a volatile impurity in cupric oxide, but no proof was afforded that the impurity was wholly driven off at the temperature of fairly bright redness. The determination of this point, as well as of the nature of the occluded material, became a matter of great importance.

#### *Tests for Impurities.*

The first hypothesis suggested was the possible imprisonment of a small amount of water.\* To subject this hypothesis to proof, pure cupric oxide might be dried at a red heat, and reduced by means of carbon monoxide, when of course any occluded water would be set free and might be weighed.

The cupric oxide used in the execution of this plan was some of that which remained from the oxygen research. It had been prepared in the usual manner. The carbon monoxide was made from oxalic and sulphuric acids, and after a preliminary purification with caustic potash the gas was collected over water in a glass gasholder. From this receptacle it was passed through very large amounts of potassic hydroxide, over calcic chloride and red hot platinum sponge, and finally through a flask containing sulphuric acid and two tubes containing phosphorus pentoxide, before being allowed to come in contact with the material to be reduced.

In Experiment 53, — which may be taken as a type, — fifteen grams of the cupric oxide contained in a hard glass tube were dried at a red heat in a stream of pure air for forty-five minutes. A small weighed phosphoric oxide tube was then connected at the exit, and the current of air was continued for over an hour.

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\* See Müller-Erbach, Jahresbericht, 1885, p. 74.



	Grams.
Weight of tube before connection	= 55.1920
“ “ after “	= 55.1922

The temperature changed from 15°.7 to 16°.8 between the two weighings, involving a correction of —.0001 to the latter weight. The tube therefore gained only the tenth of a milligram, showing the cupric oxide to have reached a constant hygroscopic condition.

During the ensuing reduction with carbon monoxide, the drying tube was again connected with the apparatus. Before the last weighing of the tube, all carbon dioxide was expelled by pure air. The tube weighed 55.2177 grams, showing a gain of 0.0255 gram, or 0.017 per cent of the weight of the cupric oxide.

Two similar experiments led to like results.

#### REDUCTION OF CUPRIC OXIDE BY CARBON MONOXIDE.

No. of Experiment.	CuO taken.	Water formed.	Volume of Carbon Monoxide.	Weight of H <sub>2</sub> O for 10 grams CuO.
	grams.	grams.	litres.	grams.
51	6.90	.0105	—	.0152
52	20.00	.0347	—	.0173
53	15.00	.0255	5.5	.0170

Nothing in these results proved that the water was not formed from the oxidation of hydrogen or hydrocarbons possibly contained in the carbon monoxide, and indeed further examination showed that it originated from this source. The metallic copper from the last experiment was immediately oxidized by a stream of pure dry air, and once more reduced with carbon monoxide. Four litres of gas required to reduce the partially reoxidized copper yielded 19.3 milligrams of water. Since this water could not possibly have come from the oxidized copper, it must have been solely obtained from impurities in the carbon monoxide. The quantity closely agreed with the amount, 18.3 milligrams, which one would have expected to find from the volume of gas used, upon the basis of previous results. Considering the fact that the volumes of gas were not very accurately measured, the difference is not greater than the experimental error. Hence it may be safely concluded that the carbon monoxide contained about four one-hundredths of a per cent of hydrogen by weight, but that the *cupric oxide retained no appreciable amount of water at a red heat.*

*Experiments 54 and 55.* — The idea that some cupric nitrate might remain undecomposed in cupric oxide is evidently not a new one, for almost every experimenter upon the subject tested for nitric acid in the water formed during the reduction. It seemed possible, however, that the nitric acid might be reduced as well as the cupric oxide, and hence that the test might not be a sufficient criterion. Accordingly, five grams of cupric oxide were dissolved in very pure dilute sulphuric acid, and several successive portions of water were distilled off from the mixture. After evaporation to small bulk in a platinum dish, the distillates were found to be neutral to methyl orange and acid to phenol phthalein. When the amount of standard alkali necessary to neutralize this acidity had been determined, hydrochloric acid was added and the sulphuric acid present was estimated as baric sulphate. Since the weight of baric sulphate (3.7 mg.) was nearly equivalent to the amount of alkali used (0.39 c. c. of a decinormal solution), since no nitric acid was found in the filtrate by the most sensitive tests, and since a very perceptible amount of copper was found there, it may be reasonably concluded that cupric sulphate had been carried over mechanically in fine drops. A second experiment yielded like results. Hence, so far as this test was concerned, *no nitric acid was to be found in cupric oxide.*

*Experiment 56.* — The tendency of various oxides to hold carbonic acid even at high temperatures is well known. Thudichum\* has observed that, in order wholly to free cupric oxide from this impurity, it is necessary to ignite it in a vacuum. In order to test this point so far as it concerns the present investigation, the following experiment was made. After a small amount of nitric acid had been added to twelve grams of cupric oxide, the substance was gradually brought to redness and maintained at this temperature for ninety minutes. The material was then rapidly transferred to a flask provided with a stoppered funnel and two bent tubes. One of the latter was connected with two test tubes containing a clear solution of baric hydroxide, and the other permitted a gentle current of air to be blown through the entire apparatus. Before either baric hydroxide or cupric oxide were added, all the tubes and flasks were of course freed from carbon dioxide. Finally, dilute boiled hydrochloric acid was run in at the funnel tube, the cupric oxide was dissolved, and the solution was gradually brought to boiling. A slight bluish precipitate of cupric hydroxide appeared after some time in the first test tube, while the

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\* Chem. Soc. Journ., 1876, [2], p. 364.

second remained perfectly clear. The excess of baric hydroxide in the first tube was quickly neutralized with weak hydrochloric acid and phenol phthalein, and the precipitate was filtered off and washed. The absence of barium from this precipitate proved the absence of carbon dioxide from the cupric oxide.

In order to test the adequacy of the method, 3.4 milligrams of sodic carbonate were added to the cupric chloride through the funnel tube. This quantity yielded only one tenth the amount of carbon dioxide necessary to account for the difference between the atomic weights of copper in question, but it nevertheless produced a heavy white precipitate in both newly filled baric hydroxide tubes. The precipitate when tested showed large quantities of barium; hence the method was quite competent to decide that *the absorption of carbonic acid by cupric oxide was not the error for which search was being made.*

*Experiment 57.* — Although it seemed very improbable that cupric oxide could contain even traces of a higher oxide after ignition at a red heat, proof of the point was not at hand. Accordingly, four grams of the substance were boiled with pure hydrochloric acid in an apparatus somewhat resembling the last one, in which all the joints were of sealed or ground glass. The vapors were driven through a reversed air cooler into bulbs containing a strong cooled solution of potassic iodide. The very small amount of iodine set free after some time was determined by means of sodic thiosulphate. This amount corresponded to 0.05 milligram of oxygen but even this was undoubtedly due to copper in uncondensed spray. Eight tenths of a milligram of potassic dichromate, subsequently added to the cupric chloride, at once set free more than double this amount of halogen in the bulbs. The method was hence shown to be adequate for the purpose. The results *prove the absence of an essential amount of any higher oxide or oxidized nitrogen from ordinary cupric oxide.*

#### *The Determination of Occluded Gases.*

After so much negative evidence, the only remaining hypothesis which could account for the irregularity of the atomic weight of copper deduced from cupric oxide is that of the occlusion of gases by the substance. This idea is by no means new. As long ago as 1842 Erdmann and Marchand\* showed that at least a small amount of air

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\* J. f. prakt. Chem., XXVI. 461.

was condensed by the substance. Frankland and Armstrong\* found in 1868 that cupric oxide prepared from the nitrate contains both carbonic acid and nitrogen. Hilditch† states that oxygen gas is occluded by cupric oxide at a red heat, and estimates the effect of this impurity upon the atomic weight of oxygen, without, however, adducing any experimental data. More recently Morley‡ has found that cupric oxide slowly gives off a gas in vacuum. It is a noticeable fact that cupric oxide is almost as serviceable as platinum in preventing bumping during ebullition.

The simplest and surest method for the liberation of an occluded gas is completely to dissolve the cupric oxide in a pure acid. It is by no means certain that indefinite heating in a vacuum would accomplish the end in view. Several pieces of apparatus more or less suitable for the present purpose were devised in succession, and by their means it was proved that some varieties of cupric oxide occlude important quantities of aeriform material. Nearly fifty determinations were made.

According to the first method a tube of the shape shown in Figure 1 was filled at the end with freshly ignited cupric oxide, and in the middle with pure boiled sulphuric acid. When the whole had been

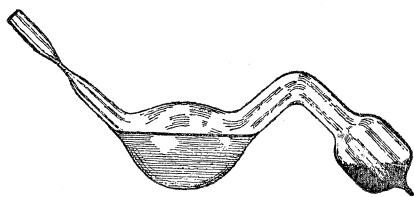


FIG. 1.

completely exhausted by means of a Sprengel pump, the liquid was allowed to come in contact with the solid, and the gas evidently set free was pumped out and measured. But the action was of course only a very superficial one, and no amount of long standing or violent shaking could accomplish a more complete change. Three experiments indicated that at least a small amount of gas, which appeared to be chiefly nitrogen, was set free. Since it was difficult to decide how much cupric oxide had been combined, the method was abandoned.

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\* Chem. Soc. Journ., XXI. 89, 93 (1868).

† Chem. News, XLIX. 37 (1884).

‡ Am. J. Sci., XLI. 231, March, 1891.

Subsequently, more dilute boiled sulphuric acid was used ; and the apparatus was sealed by fusion after exhausting, but before mixing the acid and base. The mixture was digested upon the water bath until the action was nearly or quite completed. It was found that this completion was greatly facilitated by violent shaking at the moment when the acid was poured upon the cupric oxide, for otherwise the materials inevitably formed a hard cake which dissolved very slowly. In one or two cases a small amount of unchanged cupric oxide was weighed, and subtracted from the original amount.

The apparent evolution of gas was at first very violent ; but this violence might have been partly due to ebullition caused by the heat of the chemical action. The tubes were opened under boiled water or mercury, and the gas was analyzed by means of Hempel's apparatus, somewhat modified for accurate use with very small quantities of material. The portion of the gas which was not absorbed by caustic potash, but was absorbed by pyrogallol, is tabulated below as oxygen. The remainder refused to support combustion, suffered no diminution of volume upon the addition of oxygen, and appeared perfectly inert ; hence it was undoubtedly nitrogen. In order to test the solution of pyrogallol, analyses of air were made from time to time, with satisfactory results. The volumes were of course corrected for temperature and pressure, as well as for the tension of aqueous vapor, before the weights of gas were calculated. The conditions varied so little from the mean, 24° C. and 760 mm., that a statement of these data seems inessential.

The occlusion of an inert gas by cupric oxide was so peculiar a phenomenon that many experiments were needed to carry conviction. Several blank experiments were tried, in order to test the freedom of the acid from dissolved air. The fact that only a very small amount of gas was evolved in the second experiment is also valuable evidence upon this point.

The material used in Experiments 58, 63, and 64 was four years old, while that used in Experiments 59, 65, 66, and 67 had been recently prepared. Both of these samples were made from cupric oxynitrate, whereas the one used in Experiment 61 was precipitated by caustic alkali. The tubes of Nos. 64 and 67 were opened under mercury. In No. 64 the cupric oxide was cooled for forty-eight hours after igniting, while in No. 66 the oxide was still very hot when introduced into the tube.

## OCCLUDED GAS IN CUPRIC OXIDE.—FIRST SERIES.

No. of Experiment.	Weight of Cupric Oxide.	Vessel employed for Ignition.	Temperature of Ignition.	Vol. of Gas evolved uncorrected.	Vol. of O <sub>2</sub> for 1 grm. of CuO.	Vol. of N <sub>2</sub> for 1 grm. of CuO.	Per Cent of Gas in CuO by Weight.
58	grams. 4.35	Porcelain	Dull red	cub. cent. 2.70	cub. cent. 0.03	cub. cent. 0.59	0.075
59	3.12	{ Double xble Platinum	Bright red	0.30	0.01	0.09	0.012
60	Blank		—	0.10	—	—	—
61	1.20	—	Not ignited	3.5 of CO <sub>2</sub>	Trace	Trace	—
62	Blank	—	—	0.10	—	—	—
63	1.20	Porcelain	Dull red	0.73	0.03	0.58	0.073
64	2.20	"	"	1.34	0.03	0.58	0.073
65	2.00	"	"	0.8±	Trace	0.40	0.05±
66	3.20	{ Double xble Platinum	"	1.70	0.05	0.48	0.064
67	2.10		"	1.13	0.00	0.53	0.065

The series was discontinued because a new method had been devised which was much less tedious and much more direct in its execution. According to the new method, the cupric oxide to be analyzed was introduced into a tube shaped in the manner shown in Figure 2.

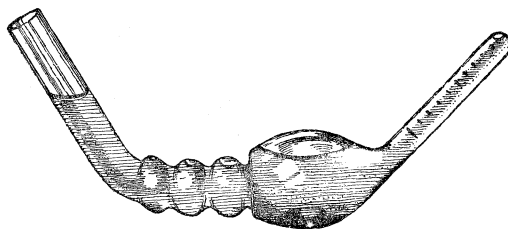


FIG. 2.

After the bulbs had been nearly filled with thoroughly boiled warm water, the open mouth of the tube was connected with an air pump to remove any mechanically adhering air. The water was usually allowed to boil for several minutes under the reduced pressure. The air was then readmitted, and the tube was entirely filled with pure boiled water, being placed perpendicularly for the purpose. When the tube had been returned to its usual position, acid was added through a fine

funnel tube in such a manner that it at once attacked the oxide. A short piece of glass rod in the large bulb together with constant agitation prevented the formation of cakes.

In the most carefully performed experiments the sulphuric acid as well as the water was boiled, but repeated trials showed this precaution to be unnecessary. In one blank experiment even ordinary distilled water and sulphuric acid evolved only about one thousandth of a cubic centimeter of gas, while boiled water, which was invariably used in the determinations, gave no trace even of the finest bubbles with unboiled sulphuric acid.

The gas evolved on the solution of the cupric oxide was collected chiefly in the largest bulb. The amount collected in the smaller bulbs decreased in proportion with the increase of distance from the first, and only a very small amount was lost through the open mouth. The gas was measured in the right hand graduated tube, or drawn off for analysis through a rubber connector attached at this end.

The apparatus was afterwards modified to avoid the slight loss through the open mouth. It then consisted of a small stoppered flask with two concentric funnel tubes, and a delivery tube closed with a rubber connector and a pinch cock. When the whole apparatus had been filled with boiled water through the larger funnel tube, the smaller one was filled with pure sulphuric acid and quickly placed inside the larger one. Upon inclining the flask, it is evident that the loss of minute bubbles must have been reduced to a minimum, while the small annular opening between the funnel tubes was quite sufficient to allow the escape of the displaced water. The gas was readily drawn off for analysis through the delivery tube, which just penetrated the smooth rubber stopper.

Many varieties of cupric oxide were examined. Material obtained from the carbonate, or by precipitation from the sulphate, evolved little or no gas, thus affording an admirable proof of the purity of the acid and water. Check experiments with such material were accordingly made from time to time. Other circumstances being equal, the purer the oxide, the more gas was evolved. Solid impurities, such as alkaline salts, seemed partially to prevent the occlusion.

The volumes of gas are given without any correction, the temperature and pressure remaining so nearly constant that the observations are not recorded. The following table is intended only as a basis of rough comparison. The gas was frequently analyzed, with results similar to those tabulated above. The results confirm those of the preceding series.

## OCCLUDED GAS IN CUPRIC OXIDE.—SECOND SERIES.

No. of Exp't.	Nature of Cupric Oxide.	Weight of CuO.	Heat and Time of Ignition.	Volume of Gas evolved.	Per Cent of Gas in CuO by Weight.	Remarks on Method.
68	Blank exp't.	grams. —	—	cubic centim. 0.00	—	H <sub>2</sub> SO <sub>4</sub> +H <sub>2</sub> O
69	" "	—	—	0.00	—	" "
70	Precipitated	1.00	Dull red	0.10	0.011	Bulbs.
71	"	1.60	"	0.20	0.013	"
72	From Carbonate	1.50	Dull red	0.07	0.006	Bulbs.
73	" "	2.00	{ Dull red ex- posed to air }	0.10	0.006	"
74	{ Crude, of Commerce, contained Cuprous Oxide. }	3.00	Not ignited	0.70	0.026	Bulbs.
75		8.00	Dull red	2.00	0.028	Flask.
76		7.00	Not ignited	2.00	0.032	{ Another sample. }
77	From Carbonate	1.50	Dull red	0.05	0.003	Flask.
78	{ Six Experi- ments with CuO prepared by action of CuO on Cu(NO <sub>3</sub> ) <sub>2</sub> & subsequent ignition of basic nitrate }	1.70	Very low	0.34	0.023	Flask.
79		3.20	Dull red, 3 hrs.	1.03	0.036	"
80		1.20	Dull red, 7 hrs.	0.25(?)	0.023(?)	"
81		1.70	Bright red	0.09	0.006	"
82		2.00	Dull red	0.26	0.015	{ Pump not used. }
83		2.00	Dull red	0.73	0.041	{ Pump not used. }
84	After Hampe's method	0.39	310°; 2 hours.	0.17	0.050	Bulbs.
85	" "	1.10	" "	0.30	0.035	"
86	" "	1.82	600°; 2 hours.	1.35	0.084	Flask.
87	" "	0.39	700°; ¼ hour.	0.30	0.087	Bulbs.
88	" "	0.50	600°; 1 hour.	0.33	0.077	"
89	" "	0.60	600°; 4 hours.	0.41	0.079	"
90	" "	0.61	" "	0.36	0.070	Used HCl.
91	" "	0.44	" "	0.29	0.079	Bulbs.
92	New preparation	2.00	700°; ¾ hour.	1.37	0.080	See below.
93	" "	2.98	600°; 2 hours.	2.12	0.082	Flask.
94	" "	0.98	See below.	0.75	0.088	See below.
95	" "	0.50	900°; 1 hour.	0.17	0.039	
96	{ From Carbon- ate prepared from Nitrate }	0.65	600°; 1 hour.	0.09	0.016	
97		0.50	290°.	0.10	0.023	
98	{ From Carbon- ate of Com- merce }	1.00	600°; 1 hour.	0.10	0.011	
99		0.75	" "	0.03	0.004	
100	Wire form	1.00	—	0.01±	0.001±	{ Contained Cu <sub>2</sub> O. }



The higher temperatures recorded above are merely approximate guesses. 600° signifies a dull red heat, 700° a medium red heat, and 900° a very bright red heat. In Experiment 92 the oxide was heated at the highest temperature obtainable by a Berzelius spirit lamp. In No. 94 the material was heated for an hour and a half in the Berzelius lamp, and then for an hour in a glass tube under a stream of oxygen. The oxide was transferred while warm to the bulb apparatus. It evolved upon solution 0.088 per cent of gas, one eighth of which was oxygen. In the ninetieth experiment hydrochloric acid was used for the solution of the oxide.

The two series of determinations, which were perhaps more numerous than necessary, showed the following important facts:—

First, that cupric oxide prepared by the ignition of the oxynitrate after Hampe's method contained between four and five times its volume of occluded gas. (Nos. 58, 63–67, 84–94.)

Second, that ignition of the oxide at very bright redness was capable of expelling a portion of this gas. The temperature required was nevertheless considerably above that which Hampe apparently employed. (Nos. 59, 81, and 95.)

Third, that beyond a certain limit the time of ignition makes no important difference. (Nos. 86–91.)

Fourth, that the gas was not absorbed from the air on cooling. (Nos. 64, 65, 66, and others.)

Fifth, that specimens of cupric oxide prepared in different ways contained very different amounts of gas. It is a curious fact that material which has been heated only to 300° contained less gaseous nitrogen than that which had been ignited at a higher temperature. In this case the nitrogen may still have existed in the combined form. (Nos. 78, 79, 84, 85.)

An explanation for the observed phenomena must necessarily be hypothetical, and will not be attempted at present.

In order to find the direct connection between the loss of weight noticed upon heating cupric oxide and the quantity of gas retained by the substance, the following experiment was made.

*Experiment 101.*—Cupric oxide which had been heated to constant weight at dull redness was ignited at bright redness in a double platinum crucible.

	Grams.
Weight of platinum crucible	= 18.0889
“ crucible + CuO, 2½ hours at dull redness	= 19.65852
“ “ “ 4 hours more “	= 19.65846
After ignition at very bright redness (20 minutes)	= 19.6574
“ “ “ “ (50 m. more)	= 19.6571
Total loss of weight	= .0014

One gram of this specimen was shown to contain 0.00081 gram of occluded gas before ignition, and 0.00039 gram afterward (Experiments 86 to 95). In the quantity taken above this difference corresponds to a loss of weight of nearly 0.0007 grams, or about half of that observed. The remainder of the loss may have been due to a partial reduction of the oxide. (Compare page 275.)

*Experiment 102.* — In order to discover if heating cupric oxide in a vacuum produced any important evolution of nitrogen, six grams of cupric oxide were dried in a glass tube with the greatest care, exactly after the manner of Hampe, and weighed in the air. One end of the tube was then sealed, the other was attached to a Sprengel pump, and the whole was heated to about 500° C. for half an hour. Upon sealing and weighing; the loss of weight was found to amount to 4.4 milligrams. The amount of air displaced was found by opening the tube under boiled water, which wholly filled it. The weight of water, reduced to 4°, was 3.48 grams, while the temperature and pressure of the air at the time of weighing the exhausted tube were respectively 24° C. and 754 mm. Hence the weight of displaced air must have equalled 4.1 milligrams, or only 0.0003 gram less than the loss of weight actually observed. Therefore the cupric oxide could not have lost more than 0.005% of its weight under the treatment described.\* The moist cupric oxide yielded approximately the usual volume of nitrogen upon solution in acids; but no very accurate measurement was made.

It has been said that these experiments were intended only for rough comparison. Since it appeared possible to apply a corresponding correction to the atomic weight of copper deduced from the oxide, it became important to make a more accurate series of determinations. The cupric oxide used in these final experiments represented three different specimens, similar to or identical with those used in Nos. 43, 45, 48, and 49.

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\* In Experiment 50 the temperature of ignition was somewhat higher.

## OCCLUDED GAS IN CUPRIC OXIDE. — THIRD SERIES.

Number of Experiment.	CuO taken.	Gas evolved. [Apparatus.]	Temperature of Gas.	Atmospheric Pressure.	Per Cent of Nitrogen in CuO by Weight.	Per Cent of Oxygen in CuO by Weight.
103	grams. 1.84	cubic centimeters. 1.38 (bulbs)	Centigrade. 25°	millimeters. 757	0.080	0.003
104	1.80	1.55 (flask)	22°	763	0.094	0.004
105	1.30	1.10 (bulbs)	24°	760	0.090	0.004
Average . . . . .					0.088	0.004

The cupric oxide of the last determination was ignited for three hours in a stream of air, and for twenty minutes in a stream of oxygen, at a medium red heat. It was impossible to determine whether the material had reached constant weight, for the hard glass tube in which the ignition was conducted was very much altered by the heat.

As might have been expected, the very pure cupric oxide employed in these experiments contained a slightly greater amount of occluded gas than the less carefully prepared material of the earlier experiments. Since the latest samples of material were precisely similar to those used in the quantitative analysis of cupric oxide, it is fitting that the latest correction should be applied to those quantitative results. The 2.97909 grams of cupric oxide used in Experiments 48 and 49 (page 277) must have contained 0.00276 gram of occluded gas. That is to say, 2.97633 grams of pure cupric oxide correspond to 2.37811 grams of metallic copper. The difference between these weights now really represents the weight of combined oxygen present. The atomic weight of copper upon this basis is easily found to be 63.605.

Correcting the indirect results from the synthesis of cupric sulphate in the same way (see page 276) the number 63.603 is obtained. Averaging this result with that immediately above, the value 63.604 is found as a mean of five determinations including two wholly distinct methods.

Since it is impossible to learn exactly the amount of gas occluded by Hampe's cupric oxide, the correction of his results will not be attempted. The residue left after the ignition of cupric sulphate can hardly contain any nitrogen; and this supposition more than accounts for the difference between the results of Baubigny's analysis and the present syntheses of cupric sulphate (see page 275).

Upon referring to the other work upon the atomic weight of copper, it is apparent that nearly all of the discrepancies have been explained. A portion of Millon and Comaille's work consisted of weighing the water formed by the reduction of cupric oxide; the reason of the low result of this part of their work is not even now evident, but at the present day a discussion of the possible causes of its error would be unprofitable. Shaw's recent result, which formerly ranked among the highest of the observed values, now appears among the lowest.

Evidently the occlusion of nitrogen by cupric oxide must have a very serious effect upon experiments in which oxygen is determined by the loss of weight of material prepared by the ignition of the basic nitrate; notably in the determination of the atomic weight of the element after the method of Dumas. When the oxide is obtained by the ignition of the metal in oxygen, the correction is of course inapplicable. Unfortunately, most of the experimenters upon the subject have omitted to state the source of their cupric oxide. The preparation used in the later experiments of Erdmann and Marchand\* must have contained nitrogen; and it will be remembered that the second series of his results gave a much higher result than the first.

In view of the correction, it is remarkable that the resultant atomic weight of oxygen in this case was not even higher than 16; for the correction is about five times as large as the amount necessary to account for the difference between 15.87 and that figure. From a difference either in the mode of preparation or in the temperature of ignition, the oxide used by Erdmann and Marchand must have contained much less nitrogen than the amount found in Experiments 103 to 105; or else some opposite error must have partially counterbalanced this one. Considering the remoteness of all the experiments, a present discussion of the results is unnecessary; but the conclusions are at least sufficient to throw a serious doubt upon the applicability of cupric oxide for a quantitative source of oxygen, as well as to support the modern low atomic weight of that element. The presence of nitrogen could not seriously influence the results of Keiser or those recently obtained here; and it is evident that the material used by Noyes could have contained no occluded gas.

The use of cupric oxide prepared from the nitrate must also introduce a serious error into organic nitrogen determinations after the method of Dumas, as Frankland and Armstrong have already pointed

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\* J. für prakt. Chemie, XXVI. 461.

out. The usual "wire form" of cupric oxide is not subject to this cause of inaccuracy, however.

In the near future other oxides will be investigated at this laboratory with regard to their possible occlusion of gases.

#### IV. UPON TYPICAL COPPER.

It has been noticed that most of the calculations described in the present paper have been referred to electrolytic copper. Whether such copper represents the typical element or not is a most important question, but is one which unfortunately cannot be conclusively answered here.

Many authorities have discussed the subject,\* and both sulphur and occluded gases have been found in metal prepared in this way. Hampe has shown that the occasional presence of sulphur is probably due to minute drops of solution imprisoned between the electrode and the deposit. When pure copper was to be prepared in the present investigation, the metal was invariably detached from the dish in order to prevent such imprisonment. In the determination of copper already in solution, the current was always made as weak as possible in order to avoid the chance of error. Besides, it will be remembered that there was a slight loss rather than a gain during electrolysis.

The occlusion of gases is at worst very slight. In order to reduce the error from this cause to a minimum, the crucible which formed the negative electrode was usually coated beforehand with copper, that the initial and the final surface might be subject to the same error. To determine the amount of volatile material absorbed by electrolytic copper, very thin strips were ignited in a stream of hydrogen, with the following results:—

		Gram.
107	0.80565 gram lost	0.00005
108	0.67724 " "	0.00004
109	1.24158 " "	0.00004
110	0.80712 " "	0.00001
111	1.00616 " "	0.00003
	Average 1 gram lost	0.00003

This correction is too small to be applied, even supposing that the method of precipitation just mentioned did not render the application

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\* Soret, *Compt. Rend.*, CVII. 733, CVIII. 1298; Hampe, *loc. cit.*; also MacIntosh, Classen, Foote, Smith, and many others.

unnecessary. The amount of hydrogen absorbed even by copper reduced from the oxide is exceedingly small. Erdmann and Marchand found that one gram of copper absorbed three one-hundredths of a milligram of hydrogen, and Dumas's results were essentially the same.\* Hampe was unable to find a trace of the gas in the copper remaining from his experiments. While this correction may have a sensible effect upon the old atomic weight of oxygen, it cannot seriously effect the atomic weight of copper.

No method for the preparation of pure copper has been suggested which is not open to possible objections. The present standard of reference has the merit of simplicity. Moreover, the results of the analysis of cupric sulphate, unless concealing some unknown error, show that electrolytic copper cannot be very different from the typical element as it exists in combination, otherwise the summation of the results would not so nearly equal one hundred per cent. Again, cupric oxide gives essentially identical results, whether analyzed by reduction or by electrolysis. It must be remembered that, while some of the copper used in the present series of researches came from Lake Superior, the greater part was prepared from "chemically pure" German cupric sulphate. Some unknown constant impurity may have vitiated all the preparations, but the present evidence seems to show that pure electrolytic copper is as definite a substance as most of the other "elementary substances" to which our atomic weights are referred.† A more elaborate comparison of copper from different sources and different modes of preparation would nevertheless be one of considerable interest.

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\* *Ann. Chim. Phys.*, [3], VIII. 189, 205. See also Thudichum and Hake, *Jahresber.* 1876, p. 966; and Johnson, *Jahresber.* 1878, p. 286.

† Grünwald and Brauner have independently come to the conclusion that copper is a compound. If this is the case, the compound must be a very definite one. See *Chem. Soc. Abstracts*, 1890, p. 434.

## V. SUMMARY OF RESULTS, 1887 TO 1891.

*The Atomic Weight of Copper.*

O = 16.000.

	Ratio.		Result.
I.	2 Ag : Cu	Eleven Determinations	63.601
II.	2 AgBr : Cu[Br <sub>2</sub> ]	Three “	63.609
III.	2 Ag : Cu[Br <sub>2</sub> ]	Three “	63.605
IV.	[CuSO <sub>4</sub> — Cu] : Cu	Three “	63.593
V.	Na <sub>2</sub> CO <sub>3</sub> : Cu	Seven “	63.600
VI.	Na <sub>2</sub> SO <sub>4</sub> : Cu	Four “	63.607
VII.	Na <sub>2</sub> CO <sub>3</sub> : [CuSO <sub>4</sub> — SO <sub>4</sub> ]	Two “	63.621
VIII.	Na <sub>2</sub> SO <sub>4</sub> : [CuSO <sub>4</sub> — SO <sub>4</sub> ]	Three “	63.641
IX.	BaSO <sub>4</sub> : Cu	One “	63.603
X.	BaSO <sub>4</sub> : [CuSO <sub>4</sub> — SO <sub>4</sub> ]	One “	63.625
XI.	[CuO — Cu] corrected : Cu	Five “	63.604
	General Average of the eleven Series		63.610
	“ “ of forty-three Determinations		63.606

Of these results five — namely, I., II., III., V., and VI. — are incomparably more trustworthy than the others. Their computation involves only very accurately determined elements, and they are least affected by a given change in the molecular weights of the standards of reference. Their experimental errors are far smaller than those of any of the others, and they involve the simplest and most direct processes, and the minimum number of necessary corrections. They are in no case computed by the objectionable method of difference. Finally, each one of the five is wholly independent of the weight of any copper compound whatsoever. These reasons constitute a sufficient ground for the separation of such results from the others.

*Selected Series.*

	Ratio.	Salt decomposed.	If O = 16.000, Cu =
I.	2 Ag : Cu	AgNO <sub>3</sub>	63.601
II.	2 AgBr : Cu	CuBr <sub>2</sub>	63.609
III.	2 Ag : Cu	CuBr <sub>2</sub>	63.605
V.	Na <sub>2</sub> CO <sub>3</sub> : Cu	CuSO <sub>4</sub>	63.600
VI.	Na <sub>2</sub> SO <sub>4</sub> : Cu	CuSO <sub>4</sub>	63.607
	Final average		63.604

If the oxygen is taken as 15.96, copper becomes 63.44. With oxygen 15.87, the value sinks to 63.09.

The mathematical discussion of these results is omitted, because it gives an exaggerated notion of the accuracy of the final average. The real probable error of this average is much more dependent upon the chemical purity of the electrolytic copper than upon the mere mechanical or experimental error with which alone the theory of least squares is competent to deal.

It is apparent that any one of the methods, thoroughly investigated, would have long ago afforded a fairly accurate knowledge of the atomic weight. Too much cannot be said against the multiplication of incomplete or carelessly obtained data; for such data carry with them not only uncertainty and confusion in the present, but also additional labor for a reviser in the future.

In the present investigation every reaction was assumed to involve some constant error, and every substance was assumed to contain some constant impurity, until a proof of the contrary was obtained. The research consisted, in fact, of a succession of mutual checks. The attempt was made to adopt precautions of a consistent order of refinement; and the still remaining causes of possible error have been carefully pointed out in the description. The not inconsiderable outlay of time, thought, and labor has been more than repaid by a conviction of the definiteness of the combining proportions which four years ago would have seemed to the writer impossible.